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NASA Aerospace Flight Battery Program

Part 1 - Volume I

Generic Safety, Handling and Qualification Guidelines for Lithium-Ion (Li-Ion) Batteries

Availability of Source Materials for Lithium-Ion (Li-Ion) Batteries

Maintaining Technical Communications Related to Aerospace Batteries (NASA Aerospace Battery Workshop)

July 10, 2008

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Report Approval and Revision History

NOTE: This document was approved at the July 10, 2008 NRB. This document was submitted to the NESC Director on October 9, 2008 for configuration control.

Approved:	Original signature on file. RR _____ NESC Director	10/9/08 _____ Date
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Revision	Description of Revision	Author	Effective Date
1.0	Initial Release	Michelle A. Manzo (GRC)	July 10, 2008

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Volume I: Technical Assessment Report

1.0 Notification and Authorization

This NASA Aerospace Flight Battery Systems Working Group was chartered within the NASA Engineering and Safety Center (NESC) on October 5, 2006. Under this charter the NASA Aerospace Battery Working Group was authorized by Mr. Ralph R. Roe, NESC Director, at the NESC Review Board (NRB) to develop an annual plan to address critical battery related issues for the agency and the aerospace community.

The initial plan was presented to the board on January 25, 2007 and signed by Mr. Ralph Roe on February 13, 2007. It involves a series of tasks addressing pressing issues related to aerospace battery implementation. Michelle Manzo serves as the lead of the NASA Aerospace Battery Working Group.

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3.0 Team List

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4.0 Executive Summary

In the summer of 2006, the NESC requested that all SPRTs be solicited for proposals for Proactive (also known as Discipline Advancing) work. Guidance for proposals included the identification of tasks that address important activities that no single project may be able (or reasonably expected) to fund, but where something critical (such as fundamental understanding, a specification, basis for risk assessment, etc.) is lacking. The NASA Aerospace Flight Battery Systems Steering Committee was approached to develop a response to this request. Relevant battery system issues of concern were identified and prioritized. A group of tasks aimed at solving the most critical of these persistent Agency-wide technical problems was assembled. These tasks became the basis of the proposal (PL-07-02/06-069-I NASA Aerospace Flight Battery Systems Working Group Annual Plan) that was presented to and accepted by the NESC Board.

At the same time, the NESC chartered the NASA Aerospace Battery Working Group within the NESC. The Battery Working Group was tasked to complete these tasks and to propose proactive work to address battery related, agency-wide issues on an annual basis. In its first year of operation, this proactive program addressed various aspects of the validation and verification of aerospace battery systems for NASA missions. Studies were performed, issues were discussed and in many cases, test programs were executed to generate recommendations and guidelines to reduce risk associated with various aspects of implementing battery technology in the aerospace industry.

The reporting on these tasks has been split into the following three parts with subsections as identified below:

- 1) Recommendations for Binding Procurements
- 2) Wet Life of Nickel-Hydrogen (Ni-H₂) Batteries
- 3) Generic Safety, Handling and Qualification Recommendations and Guidelines for Lithium-Ion (Li-Ion) Batteries
 - a. Li-Ion Performance Assessment
 - b. Generation of a Guidelines Document that addresses Safety and Handling and Qualification of Li-Ion Batteries
 - i. Definition of Conditions Required for using Pouch Cells in Aerospace Missions
 - ii. High Voltage Risk Assessment: Limitations of Internal Protective Devices in High-Voltage/High-Capacity Batteries using Li-ion Cylindrical Commercial Cell
 - iii. Definition of Safe Limits for Charging Li-Ion Cells
 - c. Availability of Source Materials for Li-Ion batteries
 - d. Technical Communications Related to Aerospace Batteries (NASA Battery Workshop)

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This document focuses on the tasks related to Li-Ion cells and batteries; it is one of a series of three reporting of the results of the Battery Working Group efforts that were initiated in 2007.

4.1 Generic Safety, Handling and Qualification Recommendations and Guidelines for Lithium-Ion (Li-Ion) Batteries

Li-Ion technology is fast evolving and requires continuous monitoring and assessment to determine the ability of the technology and recent advances to meet NASA mission requirements. NASA requirements for high energy, lightweight rechargeable batteries range from missions that require very few cycles, such as launch vehicle applications, to low-earth-orbit missions that require tens of thousands of cycles. Currently, many NASA missions with more benign cycle life requirements (LRO, ST5) of 1-2 year LEO missions or 5 year GEO missions are beginning to baseline Li-Ion technology for the energy storage systems. Heritage programs (GOES and HST) with more severe life requirements, five to ten years in LEO, are continuing to use nickel-hydrogen batteries. Standardized approaches to defining, determining, and addressing safety, handling and qualification guidelines for Li-Ion batteries are needed to streamline the process for the missions. Identification of the risks associated with launching and flying this new technology must also be addressed.

Proposed Solution:

Develop standardized approaches to defining, determining, addressing safety; handling and qualification standards are needed to streamline the process for the missions. Addressing the risks associated with flying this new technology must also be ensured.

Mitigation:

The infrastructure afforded by the NASA Aerospace Flight Battery Systems Working Group was used to collaborate and formulate generic recommendations related to the implementation of Li-Ion battery technology. These recommendations address the implementation of Li-Ion battery technology for aerospace applications via the following:

- Li-Ion Performance Assessment - A formal assessment of the current status of Li-Ion battery technology
- Guidelines Document - The generation of a general guidelines document defining specific parameters that must be addressed for the safe implementation of Li-Ion battery technology
- Focused Tasks to Generate Guidance for Specific Issues - The execution of focused test activities aimed at defining specific aspects of cell/battery design or handling as they affect specific issues that have surfaced related to the implementation of this technology. Specific issues addressed as part of this assessment were the implementation of pouch cell technology in aerospace applications, the identification of safe operational parameters in extreme environments, and the identification of specific design features required to ensure the safety of high voltage/high power battery module assemblies

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A summary of the results of these tasks follows:

4.1.1 Li-Ion Performance Assessment (GRC)

A survey of existing Li-Ion battery manufacturers (both within and outside of the United States) and their capability to meet future NASA mission needs was conducted. NASA team members requested data from both industry and government with the purpose of creating a database of Li-Ion batteries and cells, which are appropriate for aerospace applications. The database describes the performance of the cells/batteries along with the reported testing that the cells/batteries have undergone (either at the manufacturer or by other government agencies). The results are currently summarized in a Microsoft Excel spreadsheet in Appendix A of Volume II. One issue that arose during the development of this database is the proprietary nature that some members of industry place on their development and testing data. Additional legal work is required to expand the participants of the study. It is recommended that the database be converted to a dynamic web-based application that can be accessed and updated on a regular basis to reflect the growing database and use of Li-ion batteries.

4.1.2 Generation of a Guidelines Document that addresses Safety and Handling and Qualification of Li-Ion Batteries (GRC)

Many NASA missions are starting to baseline the use of Li-ion battery technology for energy storage because it has better energy density than traditional alternatives. As a newer, still-evolving technology, many users and vendors are not aware of the issues that need to be addressed in using the technology in aerospace applications.

Mitigation:

A guidelines document addressing the generic qualification of Li-Ion batteries for manned and unmanned flight applications was generated. This guideline discusses a standard approach for defining, determining, and addressing safety, handling, and qualification standards for lithium-ion (Li-Ion) batteries to help the implementation of the technology in aerospace applications. Information from a variety of other sources relating to Li-ion batteries and their aerospace uses was collected and included in this document. The document discusses basic chemical information, factors that affect battery performance, battery design, hazards and controls, typical requirements for aerospace applications, cell and battery handling and procedures, and testing. References are listed that provide more detail on program-specific requirements.

The Li-Ion chemistry is highly energetic due to its inherent high specific energy and its flammable electrolyte. Due to the extreme importance of appropriate design, test, and hazard control of Li-ion batteries, it is recommended that all Government and industry users and vendors of this technology for space applications, especially involving humans, use this document for appropriate guidance prior to implementing the technology.

Additional work is continuing to determine controls and testing needed for the safe use of Li-ion batteries. In addition, continuing changes in cell chemistry that affect the safe use and handling

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of Li-ion technology are occurring that will need to be addressed. The guidelines should be revisited and revised to incorporate any newly developed recommendations.

The Guidelines Document is provided as Appendix B in Volume II of this document; it will also be published as a stand-alone document.

4.1.2.1 Definition of Conditions Required for using Pouch Cells in Aerospace Missions (JSC/JPL)

Commercial Li-Ion pouch cell technology currently achieves very high specific energies (> 220 Wh/kg) and energy densities. Some designs have demonstrated excellent specific power (> 3 kW/kg) and high packing efficiency. However, for successful long calendar life applications using Li-Ion pouch cell designs, prevention of corrosion of the laminate composite pouch material used as a sealed enclosure and the ability of the seals to maintain hermeticity under a variety of operating conditions must be addressed. This task studied both of these areas and provides recommendations related to the use of pouch cell design in aerospace applications.

Mitigation:

In-depth studies were performed to gain insight into the above areas and to provide recommendations related to the use of pouch cell designs in aerospace applications. Corrosion of the aluminum layer of the pouch material was found prevalent in the cell design developed for NASA's spacesuit battery application, for example, within 18 months of cell manufacture. The corrosion sites were found only on the stretched (butter cupped) edges of the laminate near its seal, particular near corners. This investigation into the mechanism of this corrosion phenomenon, conducted at JSC, has produced several findings. The team found that polarizing the aluminum layer of the pouch to the negative terminal of that same live cell yielded very similar corrosion sites within days on certain commercial cell designs while other designs were impervious to the corrosion. The design differences between cells that corroded and those that did not are enumerated herein. Because the pouch corrosion phenomena could not be replicated with simple experiments only involving lithium and electrolyte contained in pouch laminates, where the Al layer of the pouch is electrically connected to the Li, the team found that the corrosion mechanism found in full cells does not involve only lithium-aluminum alloying by virtue of poor electrical isolation of the negative tab seal. More components and/or different conditions are needed to initiate the corrosive attacks on the pouch. Search for root cause is still underway.

Using a photo-acoustic infrared leak detection method, the team determined the electrolyte vapor leak rates of six cell designs and performed destructive physical analysis of the best performing designs. Coincidentally, the design with the lowest leak rate per unit of energy was also the most corrosion resistant.

With the proper amount of electrolyte and design features that enable low corrosion susceptibility, the best-sealed pouch cell designs have a strong potential to provide many years of

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service in aerospace conditions and hold great promise for lighter and more compact battery solutions for certain aerospace applications. Specifically, our leak rate findings indicate that it would take an estimated 63 months for a 10 Ah cell design by LG to lose all of its free electrolyte when stored at 25 °C. Once starved of free electrolyte, cell performance of most pouch cell designs is expected to degrade as a result of lower ionic conductivity. With cell design improvements (tighter seals, more free electrolyte), estimated life of pouch cells can be improved with only small specific energy penalties.

The integrity of the pouch cell seals upon electrical and thermal cycling and possibly under hard vacuum environments was assessed. This characteristic is a function of electrolyte, type of cathode material (which dictates the charge voltage and hence the extent of electrolyte oxidation) and the pouch seal design. Furthermore, this loss of seal integrity is accelerated at high temperatures, for example, cycling at 60°C, showed clear demarcations among various cells tested. Interestingly, SKC gel polymer showed the greatest resilience to the high temperature cycling and may be expected to exhibit similar tolerance to vacuum also.

It is clear from the extensive cycle life data presented here on a few pouch cell designs, that the pouch cell design is indeed amenable to long-term cycling, especially at ambient temperatures. Some of the designs have shown cycle life in excess of 2000 cycles at 100% depth of discharge, and several thousand cycles (~ 30,000) at partial depth of discharges. At warm temperatures, however, the cycle life is more limited, due to the gaseous oxidation products from the electrolyte creating cell internal pressures enough to affect the integrity of the pouch seals. It is recommended that the selected prototype cells be tested in the anticipated thermal and vacuum environments before hand, before committing them for use. As a diagnostic, the cells may be subjected to an accelerated cycling test at a high temperature, after establishing confidence in a correlation between such acceleration and the expected cycle life at room temperature.

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4.1.2.2 High Voltage Risk Assessment: Limitations of Internal Protective Devices in High-Voltage/High-Capacity Batteries using Li-ion Cylindrical Commercial Cells


Most commercial cylindrical 18650 Li-Ion cells have two internal protective devices, namely, the Positive Temperature Coefficient (PTC) and the Current Interrupt Device (CID). The PTC protects the cells under external short and the CID protects the cells under overcharge conditions. While proven to be effective at the single cell and small-size battery levels, these devices do not always offer protection when used in high voltage and high capacity battery designs. When these 18650 cylindrical cells are connected in large multi-cell battery configurations (in series and /or parallel connections), the PTC and CID are exposed to conditions that make them unable to carry out the protective functions, as they do in single cells or small battery configurations. This is due to the withstanding voltage limitations on the PTC that cause its ignition. Under overcharge conditions, the end of charge voltage as well as the charge current play an important role in the results obtained under this abusive condition. Charge currents that would induce PTC activation, end of charge voltages that would cause PTC ignition, and uncontrollable heat generation resulting in excessive cell heating (leading to failures in the PTC, cell seals, etc.) have been observed to be reasons that inhibit the clean opening of the CID.

Mitigation:

This study provides a comprehensive report on the limitations of PTCs and CIDs and provides recommendations to mitigate the hazards caused by these limitations.

The PTC characteristics and limitations vary with cell manufacturer and these should be well studied and understood. This information is rarely provided by the cell manufacturer and therefore, should be obtained by testing. The voltage of the cell series string should not exceed the PTC voltage. For high voltage batteries, diodes added to a series string of cells can improve their safety under external short conditions. The diodes must be carefully selected and matched to cell characteristics, many of which must be determined by test. A list of recommended tests is included in Section 7.3.2.2 and Appendix K.

In high voltage and high capacity batteries, if the CID is used as a level of safety control, overcharge tests need to be carried out to confirm its safe operation. The number of cells allowed in parallel depends on the charge current. The total charge current used to charge a bank (cells in parallel) should in no way cause an increase in PTC resistance of any single cell. In other words, in the event that all cell CIDs but one have opened, the current seen by that one cell should not cause an increase in PTC resistance. CID arcing (header test only) was observed in some cases where the difference in voltage of the power supply far exceeded the end-of-charge voltage of the battery module. The CID voltage tolerance should also be well characterized. The charger voltage limit should be set such that the difference between that value and the end-of-charge voltage of the battery does not cause arcing of the CID. The main causes of failure that prevent the CID from proper activation and safing are the charge current (causing inadvertent

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PTC activation), high temperatures (causing PTC activation or uncontrollable thermal runaway), and high voltages (causing PTC ignition).

4.1.2.3 Definition of Safe Limits for Charging Li-Ion Cells

Li-Ion cells have superior discharge characteristics at low temperatures, compared to the aqueous rechargeable battery systems. Their charge characteristics, however, are relatively less impressive. During charging at high rates and/or low temperatures, for example C/2 to C at 10° C or C/5 -20°C, which are defined by the cell design features, the cells can exhibit a tendency to have metallic lithium deposited on the carbon anode – a deviation from the intercalation process that Li-ion chemistry is about. Such Li plating will have deleterious impact on the performance, reliability and maybe even safety. This tendency towards plating is a strong function of the type of anode material, cell design (electrode capacity ratio) and other manufacturer specific characteristics. The present task evaluated such combinations of charge rates and temperatures for various Li-Ion cells.

Mitigation:

A study was conducted that involved the evaluation of various chemistries for their ability to support higher charge rates without plating at different temperatures. The studies show that evidence for Li plating on charge can be found in the form of a voltage plateau about 100 mV higher than normal in the early stages of discharge. The cells tested show that the propensity for Li plating as a function of charge rate and temperature varies significantly from one manufacturer to another. As such, in order to ensure that a Li-ion battery is being operated to preclude lithium plating, it is recommended that the specific Li-ion cells and batteries of interest be tested in the expected charge regime, rates and temperatures, to look for evidence of lithium plating. It is recommended that some margin is allowed in the charge rates, since the relative electrode capacity ratios may get worse upon cycling, due to a faster degradation from the anode. Details of the procedures are outlined in Appendix L..

The test articles utilized in this study include: i) SAFT DD cells with a low temperature electrolyte (2007 pedigree, with 1.0M LiPF₆ in EC+EMC (20:80 v/v%)), ii) Yardney 7 Ah cells, with chemistry similar to the batteries on the Mars Exploration Rovers, iii) Quallion 18650 cells, iv) Quallion pouch cells of 4 Ah with three different electrolytes, v) SKC polymer cells, and vi) A123 26650 cells of 2.3 Ah. In addition, a few laboratory glass cells with carbon anodes and nickel cobalt oxide cathodes and Li reference electrodes were employed to understand the role of electrolytes on the plating characteristics. The cells were charged at different charge rates, up to C rate, at various temperatures down to -40°C, followed by discharge at the same temperatures but at constant current corresponding to C/10. The discharge profiles were examined to determine the on-set of Li plating in the preceding charge. In short the risk of lithium plating was assessed in several likely prototype cells to identify the charge conditions not conducive to lithium plating and to establish the conditions permitting such Li plating and hence need to be avoided from the performance, reliability and safety. The proposed solution is thus to stay away from such “unfriendly” regions of charge rates (and temperatures) to avoid such problems.

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4.2 Availability of Source Materials for Li-Ion Batteries

Li-ion batteries are beginning to demonstrate the long cycle life required by low-earth and geosynchronous-orbiting missions. However, Li-ion production is dominated by the commercial marketplace and performance metrics that minimize weight and volume, and improve run time at the expense of cycle life. Commercial Li-ion cells are moving away from the electrode materials that were contained in cells that provided good cycle life in the technology validation studies performed by aerospace laboratories. As a result, the source materials that produce the life required by NASA missions are becoming unavailable.

Mitigation:

To address this issue, NASA has contributed funding to the U.S. Government led effort initiated by the CIA, the DOD and the NRO. This Title 3 effort is aimed at ensuring a constant supply of the source materials that have demonstrated the long life performance required for long-life aerospace missions. NASA now has membership on the controlling board and increased visibility into any source supply issues. Under this project, a 5-year, cost share Technology Investment Agreement (TIA) was awarded to Quallion, LLC, Sylmar, California on September 5, 2006. The agreement is managed by the US Air Force Research Laboratory (AFRL/RXM)

4.3 Maintaining Technical Communications Related to Aerospace Batteries (NASA Aerospace Battery Workshop)

Continued open communications related to aerospace battery developments, implementation and issues are critical to proactive measures to address potential battery concerns. There is a continued need for an open forum specifically addressing this technical area. These communications are facilitated by providing a forum for the communication and dissemination of data/information related to developments and issues in the battery industry. The 2007 NASA Aerospace Battery Workshop was jointly sponsored by the NESC and the Exploration Technology Development Program Energy Storage Project.

Mitigation:

The 2007 NASA Aerospace Battery Workshop convened in November 2007. The workshop was attended by scientists and engineers from around the world, representing both private industry and government entities. The number in attendance was 123, which represented a 10 percent increase over the previous year. The workshop was opened with a focused session summarizing the results of the proactive tasks being performed under this assessment. The workshop is an effective forum for the transfer and dissemination of current up to date battery advances and issues and should be continued on an annual basis.

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5.0 Problem Background, Description and Assessment Plan and Proposed Solution

5.1 Generic Safety, Handling and Qualification Guidelines for Lithium-Ion (Li-Ion) Batteries

The advancement and adoption of Li-ion batteries can be facilitated by documenting a uniform approach to addressing new technology issues.

The following activities were conducted to address this task:

- Perform an assessment on the current status of the implementation of Li-ion battery technology. This includes the assembly of a catalog of cell/battery designs for consideration for aerospace applications and the generation of a database that summarizes available performance data on cells evaluated in various test regimes.
- Generate a document providing high level guidance on the implementation of Li-ion battery technology.
- Conduct focused studies to generate needed guidance on issues relevant to the implementation of Li-ion battery technology and incorporate that wisdom into the guidelines document.

Specifics related to the assessment plans for the subsections within this area follow:

5.1.1 Li-Ion Performance Assessment (GRC)

As part of a larger Li-Ion battery study, the NASA Engineering Systems Center chartered the NASA Aerospace Flight Battery Systems Working Group to conduct a survey of available Li-Ion battery technology and its capability to meet future NASA mission needs.

To accomplish this task the NASA GRC and the Aerospace Flight Battery Steering Working Group developed a list of parameters, which describe both battery/cell performance and testing experience of Li-Ion cells/batteries that are appropriate for aerospace applications. These parameters included mass, volume, chemistry, capacity along with many other cell/battery physical and chemical descriptors as well as questions regarding the cell/battery testing history.

Each cell/battery entry contains not only the description described above but points-of-contact so that additional information could be obtained if desired. Contacts were made with both cell/battery manufactures as well as government and nongovernmental users of these cells/batteries.

Each was asked to fill in the questionnaires for the database. From this collected data, a Microsoft Excel Workbook was developed with this list of parameters. The cell size was limited to those with greater than 1 A-hr capacity. The database was organized into battery and cell vendor sections as well as a customer section. This breakout allows comparisons between the vendor supplied data and that realized from the customers.

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The intent was to give NASA access to a thorough database so that they may make an educated selection of the best available technology for use in their applications. The database describes the performance of the cells/batteries, along with the reported testing that the cells/batteries have undergone, either at the manufacturer or by other government agencies.

5.1.2 Generation of a Guidelines Document that addresses Safety and Handling and Qualification of Li-Ion Batteries (GRC)

Currently, many documents exist which address different specific aspects and applications of Li-ion technology that have not been compiled into a single source for use by the community. To fulfill this task, NASA GRC used the infrastructure afforded by the Battery Working Group to generate a guidelines document that describes Li-ion battery chemistries, discusses issues associated with their performance, and provides guidelines on hazards and controls, and testing required.

The team surveyed existing documentation pertaining to the safety, use, issues, qualification, and testing of aerospace Li-Ion batteries. Documents from NASA, The Aerospace Corporation, Air Force, Army, Naval Research Laboratory, and the European Cooperation for Space Standardization were reviewed and the guidelines and recommendations pertinent to the use of Li-ion in aerospace applications were compiled into one document and expanded upon, which is included in Appendix B.

5.1.2.1 Definition of Conditions Required for using Pouch Cells in Aerospace Missions

Introduction and Background

The spacesuit battery design pursued by NASA in 2004-2005 consisted of 25 Li-Ion pouch cells, each rated at 7.4Ah, weighing 160g, with cobaltate positive, graphite negative with copper tab termination, and used a laminate pouch material, model # D-EL40EM from DNP Packaging Films. This 8.8mm thick cell was manufactured by ElectroVaya and is shown on Figure 5.1-1. Both pouch sides were stretched into a butter cup shape to achieve the volume necessary to enclose the electrode stack of the cell. The perimeter seal of the pouch was achieved by a heated clam shell sealer in a one shot process. The terminal tab isolation material was polyethylene.

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Figure 5.1-1. Electrovaya spacesuit pouch cell

In order to package 5 cells connected in parallel in a cell module that would fit the spacesuit battery box, the edges of the sealed pouch area were folded and tucked against the edges of the cell. In the corners, edges were folded over twice.

Eighteen months after cell activation, one spacesuit battery was found to have anomalous intermittent discontinuity in its discharge curve, which led us to believe that one of its cells in one certain cell module had an intermittent terminal connection. Disassembly of the battery and the suspect cell module found (Figures 5.1-2 and 5.1-3) numerous dark corrosion spots in 3 of the 5 cells of the module. All the spots were on the stretched portion of the laminate pouch material.

The team found evidence that these spots had caused electrolyte leakage into the vacuum-sealed cell module pouch enclosure. Within hours after opening that outer pouch and exposing its cells to ambient humidity, the dark corrosion spots turned into grayish spots.



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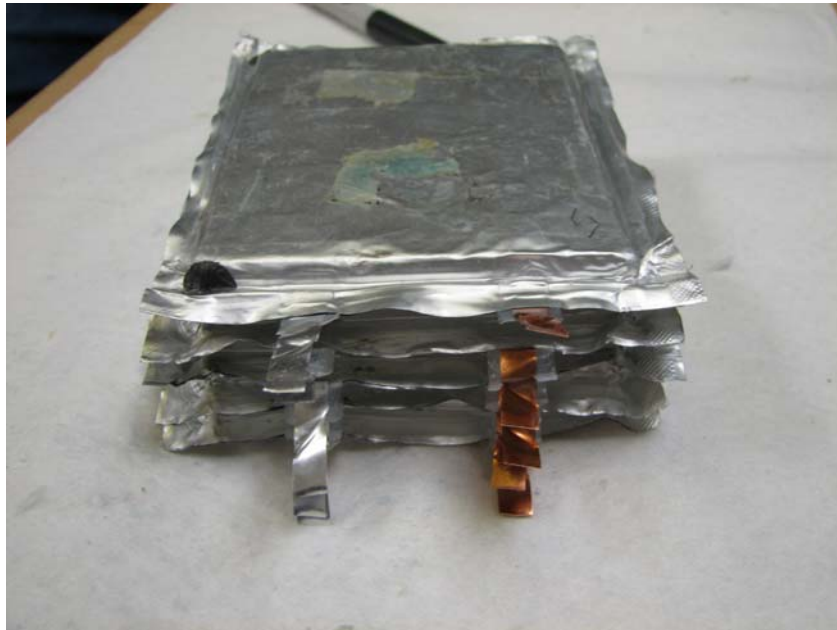


Figure 5.1-2. 5-cell stack immediately after removal of outer cell module pouch

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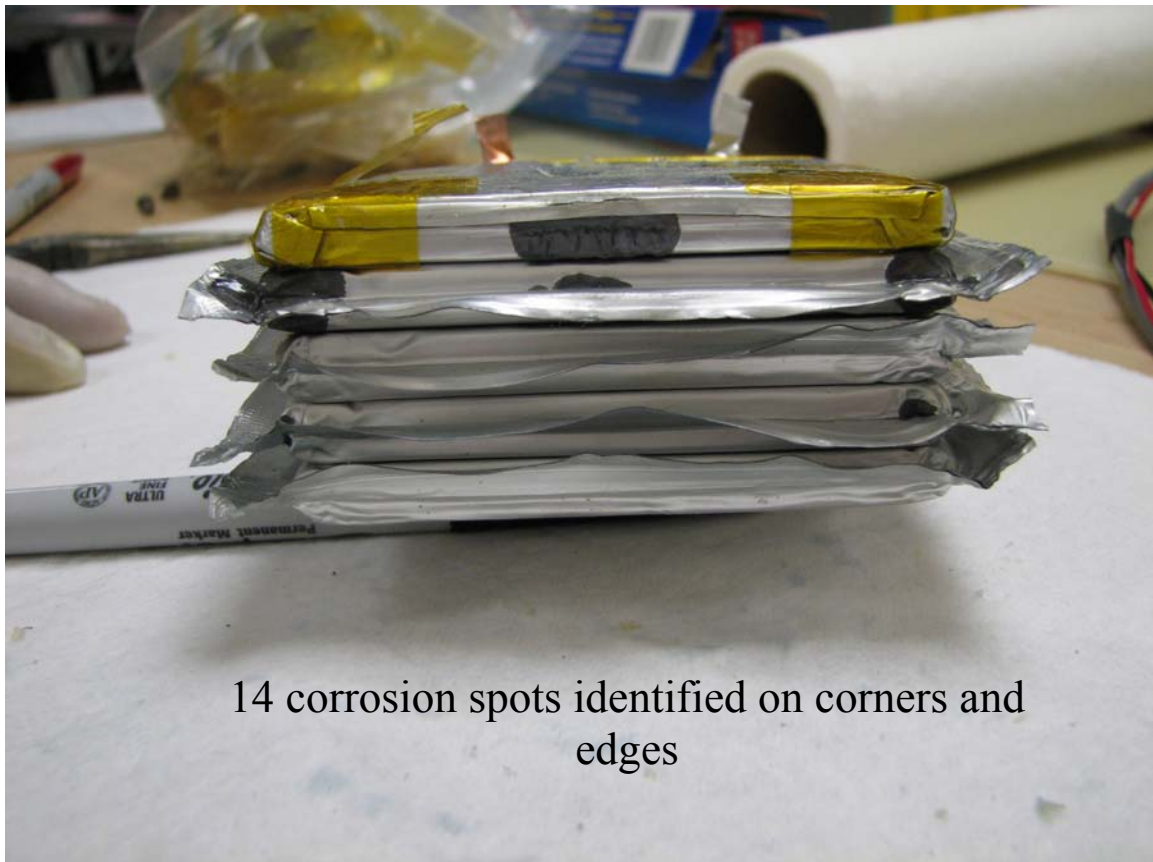


Figure 5.1-3. Disassembled cell module with dark corrosion spots minutes after opening the vacuum sealed cell module pouch enclosure

Assessment Plan:

The JSC Battery Group led the first part of this effort and it was performed by 3 members of the group at the chemical laboratory in JSC's Energy Systems Test Area (ESTA). Some portion of the work was contracted to Mobile Power Solutions in Beaverton, Oregon and Teledyne Energy in Sparks, MD.

One objective was to determine root cause of the pouch corrosion mechanism that prematurely ended the calendar life of the ElectroVaya pouch cell design for NASA's spacesuit application. Another objective was to learn which design features of a pouch cell make it impervious to corrosion. A third objective was to determine the hermeticity of the cell seals for various pouch cell designs by a Photo Acoustic Infrared (PA-IR) leak detection method and assess if cell hermeticity is a factor in corrosion susceptibility

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Investigative Method

A review of all cells produced by Electroveya after the spacesuit battery cell design had been finalized and put under configuration control found that a significant subset of 21 month old cells that were in long term storage also showed evidence of similar corrosion. More suspect spacesuit batteries were found and disassembled to find additional cases of this corrosion phenomenon. At the time, our only other cell design found to have a similar problem was a 3.8 Ah design from SKC-America. This design was intended as an alternative cell building block for the spacesuit battery. A single corrosion spot developed in 9 months of storage into a gray wart-like blemish and was accompanied with extreme puffing of the cell.

The pouch and its seals were examined by mounting in epoxy and cross-cutting them and taking photo micrographs. Significant thinning of the Al layer was found in the butter cup region of the Electroveya pouch while less relative thinning was found in the LG design, as shown in Figures 5.1-4 (a) and (b).

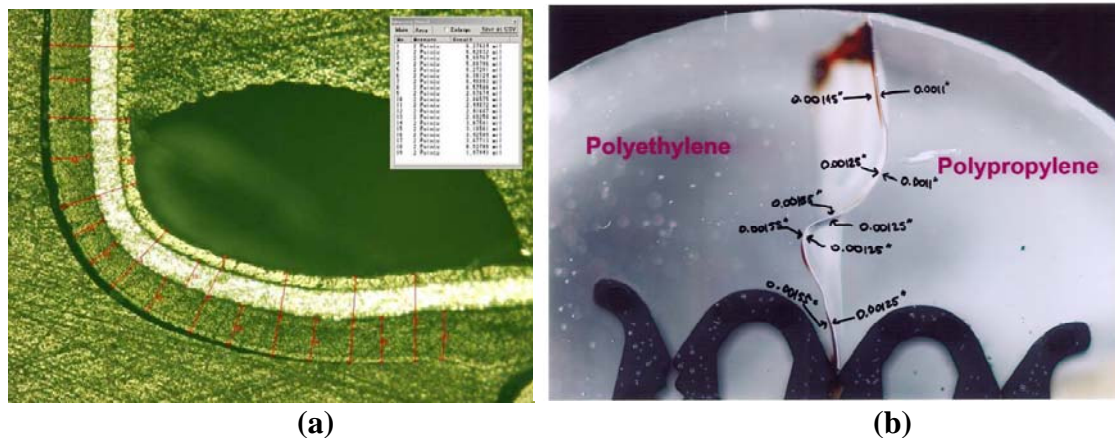



Figure 5.1-4. (a) LG pouch cross cut (b) Electroveya pouch cross cut

The corrosion spots were examined with SEM-EDS and elemental analysis found that those spots mainly consist of phosphorus compounds, mostly coming from the electrolyte salt, LiPF_6 .

Accelerated replication of the corrosion was attempted with the Electroveya cell and 4 others cell designs from other manufacturers (SKC, LG, Saehan, and Kokam). This was done by connecting the negative tab to a section of the pouch with its outer insulation removed with a solder gun to expose the inner aluminum layer. This polarizes the aluminum layer of the pouch to the negative potential.

Destructive physical analyses of healthy cells from each manufacturer were performed to determine what design features were common among the corroded and non-corroded cell designs.

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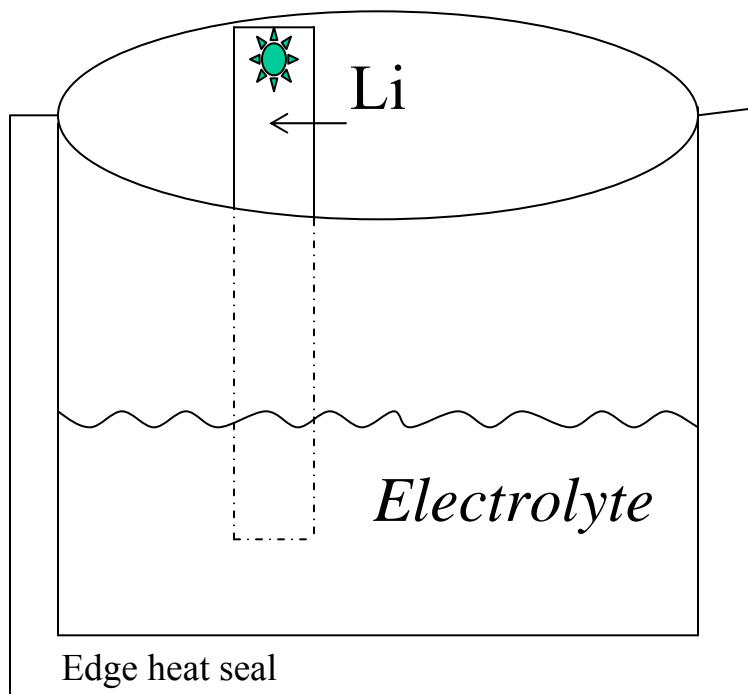
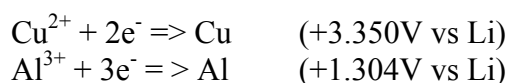


Figure 5.1-5. Pouch Boat Sketch

The team tested an aluminum-lithium alloy formation hypothesis as the pouch corrosion mechanism with simple laboratory experiments. A galvanic reaction is hypothesized between the anode and aluminum layer of the pouch once it's polarized to the negative potential due to the electrochemical potential difference between copper (anode terminal material) and aluminum.



The galvanic reaction is thought to occur at sites on the pouch aluminum layer where defects in the pouch polymeric insulation exist and are wetted with electrolyte.

The experiment was achieved by cutting the bottom half of the cell pouch from existing cells, filling the resulting “boat” half way with electrolyte (1M LiPF₆ in a 50 percent-50 percent mix of ethylene carbonate (EC) and dimethyl carbonate (DMC)), and connecting one end of a strip of lithium metal electrically to the pouch aluminum layer while immersing the other end in the electrolyte pool (Figure 5.1-5). This was all done in an Argon-filled glove box with humidity levels kept < 2 percent relative humidity.

The team used several different pouch assemblies to assemble the “boats” to discern any differences if the seals were folded, or if sealed with clam shell sealer, or if the edges of the pouch were “butter-cupped” or if none of the mentioned features existed. In addition, the lithium

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strips were replaced with copper strips and combined the two strips in replications of pouch boat experiments. After several months without success in inducing the corrosion phenomena, new boat experiments were introduced with the added feature of connecting a healthy (3.7V) cell to polarize the cell terminals. Reverse polarity was also tested with the lithium metal strip. When the lithium strip was replaced with a copper strip, it was polarized to positive 3.6V relative to the pouch aluminum layer.

The team performed photo acoustic infrared (PA-IR) leak testing of 6 cell designs, all from different manufacturers (shown in Figures 5.1-6, -7, & -8), to assess the hermeticity of their pouch seal designs. These six pouch cell designs were acceptance tested, individually sealed in aluminized heat-seal bags, thermally cycled (24 times between -40°C to +54°C with 3 hour dwell times) or left at ambient, electrolyte volatile concentration that exited the cell into the bags was determined by a photo acoustic infrared detector, and then the cells were acceptance tested again. The pre and post acceptance tests performed by Mobile Power Solutions indicated all nominal performance except for several ElectroVaya cells which demonstrated poor capacity. All other tests were performed by Teledyne Energy. The PA-IR detector was calibrated with a DEC sample of calibrated concentration to be accurate within 11 percent at the low concentration levels.

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(a) (b)

Figure 5.1-6. (a) SKC Cell (b) LG Cell



(a) (b)

Figure 5.1-7. (a) Saehan Cell (b) Quallion Cell

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Figure 5.1-8. Kokam Cell

Task II : Recommendations for Aerospace Application of Pouch Cells

The second part of this effort was led by JPL and the objective of this sub-task was to evaluate performance limitations of pouch cell designs in general in space environments, specifically thermal and vacuum environments.

Problem description

Pouch cell designs, with either liquid or gel polymer or true polymer electrolytes, offer enhanced specific energy and energy densities compared to conventional designs with metallic cell cases. They also offer better form factor and packing efficiency and thus are an attractive option for short-life missions. However, there is one shortcoming of this design, i.e., their inability to maintain hermeticity of the cell through its lifetime. This is especially the case with electrolytes have low boiling point and high vapor pressure, which cause the pouch to open. For example, the Alliant Li-gel polymer pouch cells developed for the 2001 Mars Lander application exhibited impressive specific energies of ~ 160 Wh/kg, but sustained rapid capacity fade during cycling at ambient temperature and vented after 300 cycles, (Figure 5.1-9). Prior to the venting, the charge to discharge ratio is unusually high suggesting a significant pressure build from the parasitic

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electrolyte oxidation (Figure 5.1-10). It is anticipated that exposures to high temperature operations or hard vacuum would accelerate such degradation and aggravate the problem of pouch integrity. The objective of this sub-task was to evaluate performance limitations of pouch cell designs in general in space environments, specifically thermal and vacuum environments.

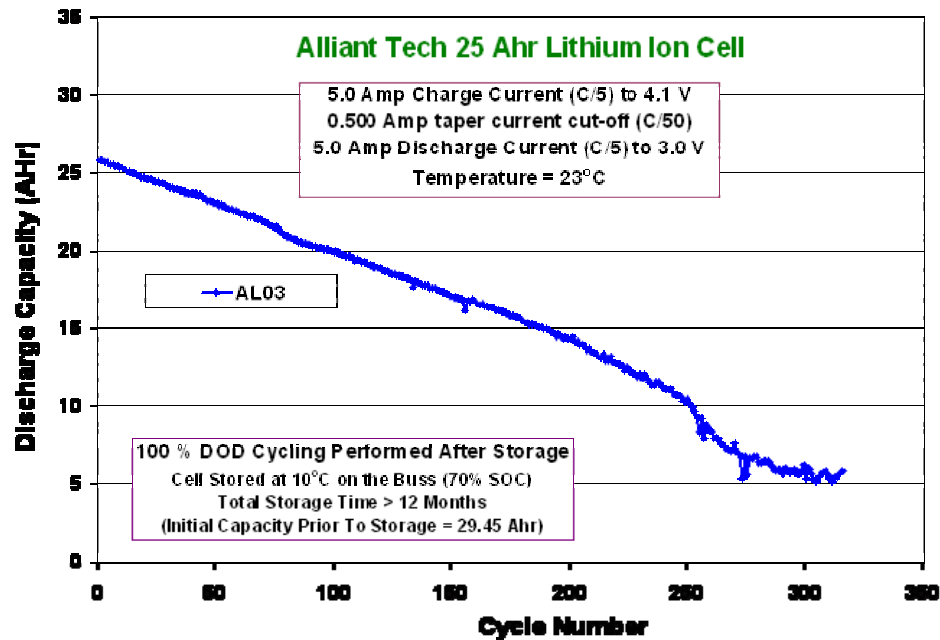


Figure 5.1-9. Cycling of Alliant Tech 25 Ah Li-Ion gel polymer electrolyte cells at ambient temperature



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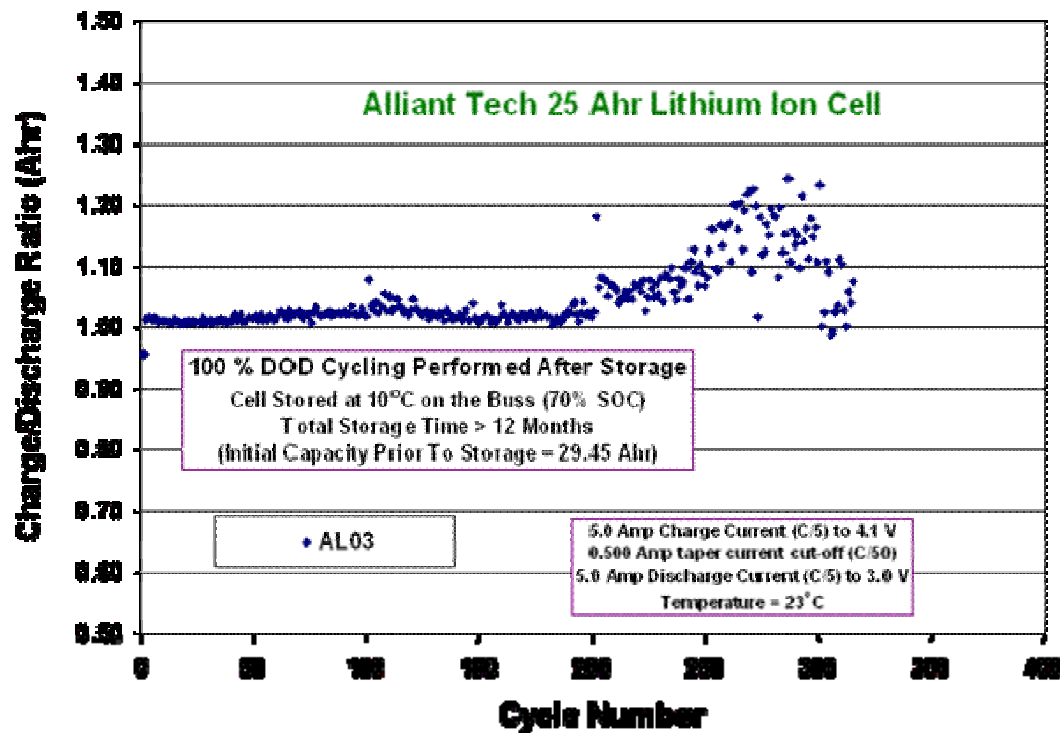



Figure 5.1-10. Charge to discharge capacity ratio during the cycling of Alliant Tech 25 Ah cell at 25°C

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Assessment Plan

A systematic study was been undertaken to determine the viability of using pouch Li-ion and Li-ion polymer batteries under conditions relevant to space applications, specifically hard vacuum and thermal cycling. The approach adopted here was to evaluate Li-Ion pouch cells, with different electrolytes and from different manufacturers for their ability to maintain hermeticity. Furthermore, adequate screening methods were developed to identify the proper test methodology.

Table 5.1-1. Various pouch cells selected for the study

Manufacturer	Type	Chemistry	
		Couple	Electrolyte
Quallion	Pouch Cells	C-Li(Mn, Ni, Co)O ₂	ED2-LT electrolyte (Quallion)
	Pouch Cells	C-Li(Mn, Ni, Co)O ₂	ED1-LT electrolyte (Quallion)
	Pouch cells	C-Li(Mn, Ni, Co)O ₂	Quallion Baseline
	Pouch cells	C-Li(Mn, Ni, Co)O ₂	Two variations of JPL Electrolytes
SKC	Pouch Cells	C-Li(CO)O ₂	Gel Polymer electrolyte (SKC)
Compact power	Pouch Cells	C-LiMn ₂ O ₄	Gel Polymer (Compact power) Also with JPL electrolytes
LTC	Pouch Cells	C-Li(Ni,Co)O ₂	Liquid Electrolyte (LTC)

The test articles utilized in this study are listed in Table 5.1-1. These include i) 4.3 Ah pouch cells made by Quallion with their baseline electrolyte, two variations of low temperature electrolytes and two variations of JPL low temperature electrolyte, ii) SKC cells with their gel polymer electrolyte, iii) Compact Power cells containing their gel polymer electrolyte as well as a few of JPL low temperature electrolytes as plasticizers and iv) LTC Li-ion cells. These cells were subjected to a thorough characterization testing, which included determining the capacities as a function of charge and discharge rates at different temperatures as well as determining the DC impedance of some of these as a function of state of charge and temperature. In addition, the LTC and Compact power cells have been well tested under 100 percent DOD and partial DOD cycling. These characterization tests were aimed at providing the baseline data prior to the thermal cycling and vacuum. Some of these cells were subjected to high temperature cycling, as a means of accelerating the failure that would occur over longer cycles at ambient temperature. In addition, the rest of the cells are being exposed to thermal vacuum cycling in the non-operating mode. Upon completion of the thermal vacuum cycles, the cells will be once again subjected to a detailed characterization to quantify their effects on the performance.

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5.1.2.2 High Voltage Risk Assessment: Limitations of Internal Protective Devices in High-Voltage/High-Capacity Li-ion Cylindrical Commercial Cells

Introduction and Background

Li-Ion cells have a very high energy density, low self discharge and no memory effect. The cells are available in a variety of shapes and sizes. The most commonly available commercial cells are the 18650, a cylindrical type. The cylindrical cells, in most cases, have at least two internal protective devices (Figure 5.1-11). These two are the PTC (Positive Temperature Coefficient) and the CID (Current Interrupt Device). The PTC protects the cell under external short conditions and the CID protects the cell under overvoltage conditions.

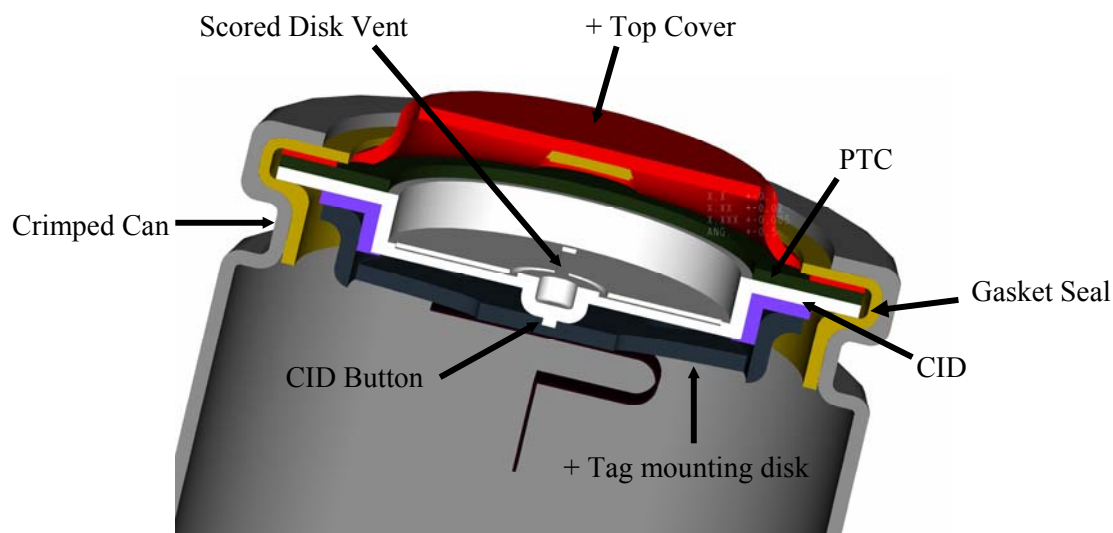


Figure 5.1-11. Cross-Section of a Typical 18650 Cylindrical Li-Ion cell showing the PTC (shown in green) and CID (shown in white)

The PTC is a doughnut shaped device that is made up of a polymer material sandwiched between two stainless steel discs. Under high current (external short) or high temperature conditions, the polymeric material expands, thus decreasing the electrical conductivity of the PTC. This reduces the current load on the cell to a value that can be handled by it. The PTC is a passively resettable device. The PTCs are very commonly found in cells with a Li-cobaltate cathode.

The other protective device internal to the 18650 cell design is the CID, which activates due to increased pressure and is not resettable, causing the cell to remain open (unusable) after activation. In some cells, as in the spinel cathodes and in those dedicated to provide high-rate performance, only the CID is present. The CID consists of two discs that are typically in

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mechanical contact with each other in one location. The electrolyte in the cells contain additives that, under overcharge conditions, cause excessive gas buildup causing one of the discs to change shape and mechanically lose contact with the other. This results in a dead (internally opened) cell, that is prevented from going into a catastrophic condition of venting and fire.

Commercial-off-the-shelf (COTS) batteries contain cylindrical cells in parallel and/or series combinations. The COTS batteries are often equipped with cell balancing, monitoring and protecting circuitry. The batteries manufactured by original equipment manufacturers are usually two-fault tolerant to all catastrophic failures, independently or in combination with the charger or equipment it powers. Monitoring of individual low capacity cells in high capacity and high voltage batteries may not be a practical solution and the battery designer may depend on the cell level controls for safety. The human-rated safety requirement for NASA applications is the presence of two-failure tolerance to catastrophic hazards. These internal protective devices in small battery configurations work very well as effective levels of safety control and can be counted as a level of fault tolerance to prevent catastrophic failures. Their effectiveness as safety controls in high voltage and high capacity battery configurations requires testing and confirmation.

Problem Description

The internal protective devices, namely, the PTC and CID, have been extremely reliable at a single cell level and have resulted in preventing the cell from reaching a hazardous condition 100 percent of the time (ref.16-19). However, test programs in the past five years have indicated that batteries built with cylindrical COTS cells in multi-cell configurations (series and /or parallel) have experienced thermal runaway under various test conditions (ref. 20). Analysis of test data indicated that the two major causes for the thermal runaway are overvoltage (overcharge) and external short conditions. Further investigation (ref. 21, 22) confirmed the existence of this problem. It was observed that the internal protective devices were either not protecting as expected or were themselves a cause for the hazards encountered. There has been confirmed evidence of PTC ignition above its withstanding (threshold) voltage causing thermal runaway under external short conditions in high voltage modules and batteries, but the overcharge catastrophes were not well understood. Under overcharge conditions in high voltage and high capacity modules, thermal runaway was observed indicating that the CIDs did not protect the cells from catastrophic events, as seen in single cells. Hence this study was initiated to understand the causes for the thermal runaway in high-voltage and high capacity battery modules and to determine the limitations of the cell internal protective devices.

Assessment Plan

The assessment plan for this task consisted of three parts. The first focused on determining the breakdown voltage limits of cell PTC devices and the arcing limits of the CID with single component and cell testing. These tests were performed at Symmetry Resources, Inc. (SRI), in Arab, AL and at NASA-JSC. Secondly, electrical abuse test of various high voltage and high capacity battery bundles of the cells were performed to determine the abuse tolerance differences

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between single cell and multiple cell batteries. These tests were conducted at Mobile Power Solutions (MPS), in Beaverton, OR. Finally, the generation of a design guideline for a diode protection scheme for high voltage battery applications using cells with PTC devices. In addition, results from past studies on the high-voltage strings under overcharge and external shorts carried out by JSC in collaboration with Applied Power International have been included for completeness of study.

Proposed Solution

Multi-cell batteries with designs that include series and parallel commercial-off-the-shelf (COTS) cell configurations should carry out extensive testing as recommended below.

For battery designs incorporating cell-level internal protective devices such as the PTC and CID as safety controls, a comprehensive understanding of the performance and limitations of both devices should first be obtained. The PTC should be tested at the single cell level to understand its trip current as well as its withstanding voltage (Appendix K). Strings and banks of cells (as required in the battery design) should be subjected to external short circuit tests to confirm that the string length and bank size do not compromise the safe activation of the PTC especially if it is used as a level of safety control.

Similarly, overcharge tests should be performed by changing the voltage and /or current to determine the limitations of the cell's internal protective devices and then by carrying out a test with the actual battery design configuration using cells and confirming that the protective devices work as expected. This is necessary especially if the CID is being used as a level of safety control.

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One method to mitigate the risks caused by inadequate protection of the PTC is to use diodes to isolate cell strings into small series modules. If diodes are placed in parallel with groups of cells as shown in Figure 5.1-12, the maximum voltage that may appear across a PTC is limited to less than the total string voltage. Reverse diodes across substrings help with other high impedance cell conditions (tripped CID, shutdown separator, discharged cell) by holding down the maximum voltage that can appear across the impedance.

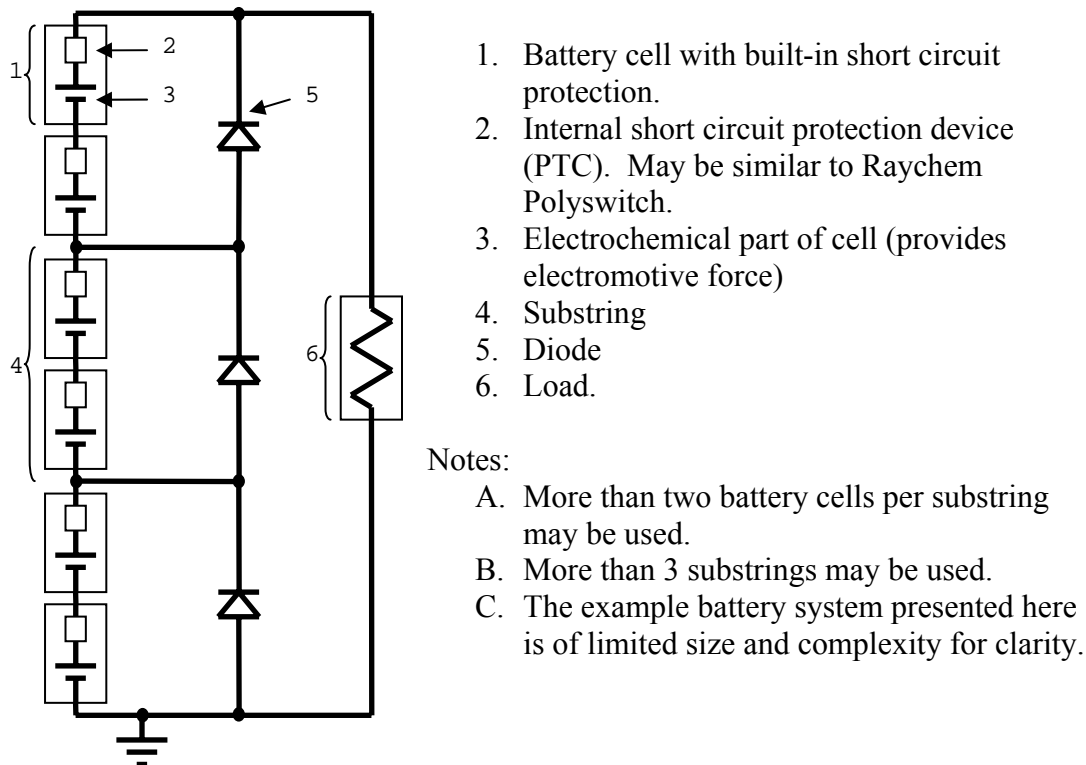


Figure 5.1-12. Diode Protection Scheme for High Voltage Battery Configurations

- Appendix G provides a report on Li-ion Cell PTC Device withstanding voltage test results and analysis.
- Appendix H provides a report on the Li-ion CID arcing tests carried out on cell headers with the addition of electrolyte and pressure.
- Appendix I provides a report on the CID arcing tests done to assess the hazard on live Li-ion cells.
- Appendix J provides an extensive database with results on external short and overcharge tests carried out on cell strings and banks of various lengths.
- Appendix K provides implementation guidelines for the diode protection scheme that can be used to mitigate the hazards caused by the PTC withstanding voltage limitation.

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5.1.2.3 Definition of Safe Limits for Charging Li-Ion Cells

Problem description

Li-Ion batteries operate over wide temperature range, typically -20 to +40°C, unlike the aqueous battery systems. However, there are constraints on their charge rates, especially at low temperatures. Due to hindered kinetics for Li intercalation, lithium tends to reduce as metal on the graphite anode. Such plated lithium may reversibly oxidize during discharge, at a lower potential than graphite or higher cell voltage, manifesting as a (high) voltage plateau, about 100 mV higher than the expected discharge voltages, as shown in Figure 5.1-13. Even though, the plated lithium is reversible or may chemically intercalate into graphite over time, its presence at the anode surface will mean an accelerated degradation of the electrolytes, reduced cycle life, reliability and may even be unsafe.

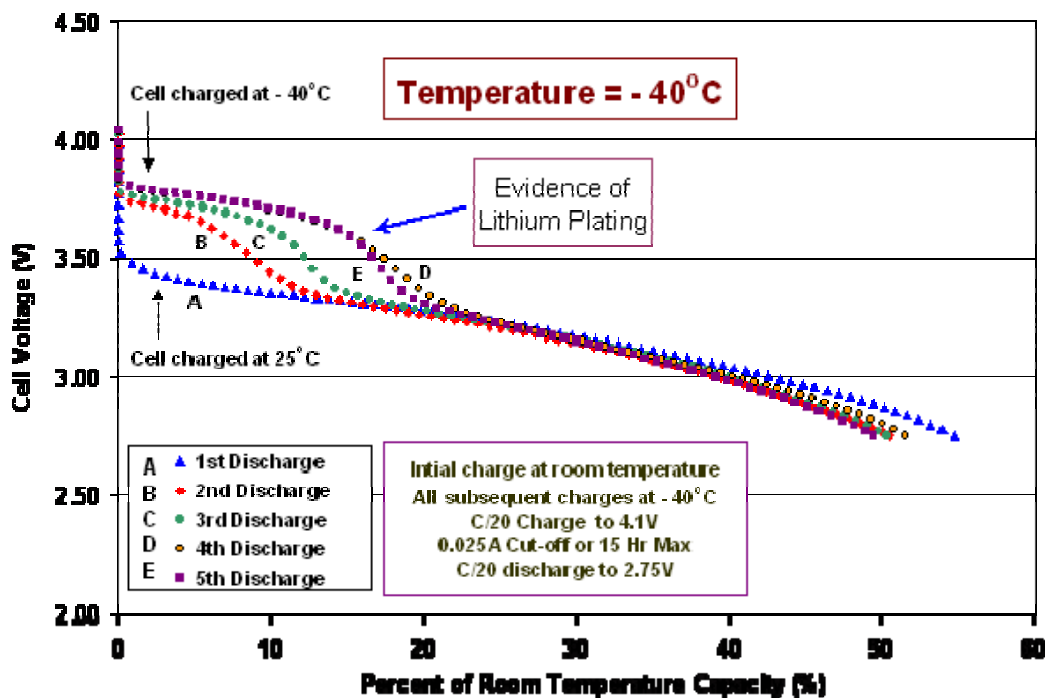


Figure 5.1-13. Discharge curves of SAFT DD Li-Ion cells at -40C, following charge at -40C. Curve represents a charge at room temperature

Assessment Plan

A systematic study was undertaken to determine conditions that ensure safe charging of Li-ion batteries under extreme conditions of charge rate and temperature, specifically at low

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temperatures. The approach adopted here was to evaluate lithium-ion cells, with different electrolytes, electrode capacity ratios and configurations from different manufacturers for their ability to support such charge rates without any adverse effects, e. g., Li plating at low temperatures. In this process adequate screening methods were developed to identify the lithium plating phenomenon

The test articles utilized in this study include: i) SAFT DD cells with a low temperature electrolyte (2007 pedigree, with 1.0M LiPF₆ in EC+EMC (20:80 v/v%)), ii) Yardney 7 Ah cells, with chemistry similar to the batteries on the Mars Exploration Rovers, iii) Quallion 18650 cells, iv) Quallion pouch cells of 4 Ah with three different electrolytes, v) SKC polymer cells, and vi) A123 26650 cells of 2.3 Ah. In addition, a few laboratory glass cells with carbon anodes and nickel cobalt oxide cathodes and Li reference electrodes were employed to understand the role of electrolytes on the plating characteristics.

The cells were charged at different charge rates, up to C rate, at various temperatures down to -40°C, followed by discharge at the same temperatures but at constant current corresponding to C/10. The discharge profiles were examined to determine the on-set of Li plating in the preceding charge. In short the risk of lithium plating has been assessed in several likely prototype cells to identify the charge conditions not conducive to lithium plating and to establish the conditions permitting such Li plating and hence need to be avoided from the performance, reliability and safety standpoint.

Proposed solution

In order to ensure that a Li-ion battery is being operated to preclude lithium plating, it is recommended that the specific Li-ion cells and batteries of interest be tested in the expected charge regime, rates and temperatures, to look for evidence of lithium plating. It is recommended that some margin is allowed in the charge rates, since the relative electrode capacity ratios may get worse upon cycling, due to a faster degradation from the anode. Details of the procedures are outlined in Appendix L.

5.2 Availability of Source Materials for Li-Ion Batteries

Problem description

Li-Ion batteries are beginning to demonstrate the long cycle life required by low-earth and geosynchronous-orbiting missions. However, Li-Ion production is dominated by the commercial marketplace which emphasizes performance metrics that minimize weight and volume, and improve safety at the expense of cycle life. As a result, the source materials that produce the life required by NASA and other government missions are becoming unavailable in the commercial market.

Proposed Solution

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The availability of source materials for Li-Ion batteries is being addressed by a U.S. Government sponsored Defense Production Act Title III project. NASA is contributing funding to support this effort that is effort aimed at ensuring a constant supply of the Li-Ion source materials that have demonstrated the long life performance required for long-life aerospace missions. The objective of this Title III project is to establish a viable domestic source of spacecraft quality rechargeable Li-Ion cells and the critical materials required to produce these cells. The project is structured as a five year, incrementally funded effort to create a supplier that is responsive to DoD requirements and capable of producing these extremely long life cells and component materials.

5.3 Maintaining Technical Communications Related to Aerospace Batteries (NASA Aerospace Battery Workshop)

Problem Description:

There exists a lack of significant, quality venues wherein aerospace battery technology issues and concerns can be discussed. Although several power-related conferences and workshops do exist, their focus is typically broad and any discussion of aerospace battery technologies is limited to a small percentage of the overall program agenda. This lack of quality venues significantly hinders the dissemination and discussion of issues that directly affect the aerospace battery industry. This, in turn, creates a risk to the development of safe, reliable, and efficient battery systems for future NASA missions.

Proposed Solution:

In an effort to mitigate this risk, it was proposed that the NESC jointly sponsor the NASA Aerospace Battery Workshop with the Exploration Technology Development Project. This will provide a consistent government/industry forum for the dissemination of data/information related to developments and issues in the aerospace battery industry.

6.0 Research Summary

6.1 Generic Safety, Handling and Qualification Guidelines for Lithium-Ion (Li-Ion) Batteries

6.1.1 Li-Ion Performance Assessment (GRC)/Li-Ion Database

All of the data collected from the vendors and government for this database resides in a single Microsoft Excel file. Table 6.1-1 shows a list of the participants who provided information in this survey. Participation levels varied with each company/organization.

This file is organized into three worksheets. The first worksheet is the Cell Vendor Survey sheet that contains information about cells and their reported performance from the vendors. Cells represented include Sony, Yardney, Quallion, and Sanyo and Saft. The second sheet shows

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various batteries some of which have been flown and others that are slated to be flown. ABSL has the largest number of space flight missions using Li-Ion batteries of those missions surveyed in this study. The last worksheet shows a summary of the government reported testing data of cells and batteries.

Table 6.1-1. Cell/Battery Database Participants

Naval Research Lab
 NASA Johnson Space Center
 NASA Glenn Research Center
 NASA Ames
 Lockheed Martin
 Quallion
 Saft
 Yardney
 Sanyo
 ABSL
 Aerospace Corporation

The database is found as an MS Excel Spreadsheet in Appendix A to this report.

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6.1.2 Generation of a Guidelines Document that addresses Safety and Handling and Qualification of Li-Ion Batteries (GRC)

No data analyses were performed for this sub-task.

6.1.2.1 Definition of Conditions Required for using Pouch Cells in Aerospace Missions

The team was successful with the accelerated corrosion replication test as described in Section 5.3.2.1, which simply consists of polarizing the aluminum layer of the pouch laminate to the negative cell terminal. Within one week, three of the five cell designs developed corrosion spots after the onset of polarizing the pouch to the negative terminal. The other two cell designs (LG and SKC) did not corrode even after nearly 6 months of testing and observation. Figure 6.1-1 shows corrosion on a Kokam pouch cell.



Figure 6.1-1. Two pouch corrosion spots on the Kokam cell

It was observed that pouch isolation from the negative terminal degrades in the days and hours prior to the initial appearance of corrosion spots. On a daily basis, the pouch to negative connection was disconnected momentarily for an isolation resistance measurement. However, after DPA, the tab to pouch seal isolation were verified to be nominal ($> 1\text{Mohm}$) in all cases and equivalent to that found before the test. This indicates that the reduced isolation resistance

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does not occur at the tab to pouch seal area and that the corrosion deposits form a conductive bridge with free electrolyte between the inner layer of the pouch and the cell stack.

Attempts to replicate the hypothesized aluminum-lithium alloy phenomena with a fundamental experiment were unsuccessful. A lithium strip connected electrically to the aluminum layer of a pouch, while immersed in electrolyte, as shown in Figure 5.1-5, did not cause any corrosion spots on any part of the pouch even after two months. Replacing the lithium with copper and adding a copper strip in contact with the lithium strip did not induce any corrosion attacks on the pouch. Neither did using pouch material that had or had not been butter cupped, clam shell sealed, and/or folded did not induce any corrosion, nor did placing a 3V voltage source between the aluminum and the lithium strip. This strongly suggests that something else is needed to trigger the corrosion mechanism. Maybe, the electrode materials are needed.

The pouch of a Kokam cell was polarized with its pouch seal intentionally breached at a corner and with spacing imposed between the large flat pouch surfaces and the cell electrode stack. These conditions did not prevent the occurrence of corrosion. This leads to the conclusion that stack compression or maintenance of a vacuum seal was not needed for pouch corrosion to occur.

SEM/EDS analysis of the gray spots generated in the Electrovaya cell design found spots to form in a deposit shape on the internal side of the pouch. The deposit looks like one layer of corrosion products slowly built on the next layer. The resulting “mound” of deposit is sufficiently large to electrically bridge to the electrode stack and could have caused the lowering of pouch isolation that was found to precede the visual appearance of corrosion spots on the outside of the pouch. Figure 6.1-2 shows one of the large deposits on the inner side of the pouch perimeter seal.

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Figure 6.1-2. Corrosion “mound” found on the cell stack side of the pouch perimeter seal.

To compare the hermeticity of various pouch cell designs, the Photo Acoustic Infrared (PAIR) leak rate determination method was employed. It relies on IR light excitation of the most volatile component of the electrolyte solvent to generate an acoustic signal that is proportional to that component’s concentration. The advantages of the method over helium leak detection method are that it measures directly the escaping component of the cell electrolyte and does it without forcing foreign molecules (He) into the cell. The disadvantage is that takes longer to get an accurate measurement. Results are found in Table 6.1-2. Details of the PAIR testing can be found in Appendices C, D and E.



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Table 6.1-2. Cell Design and Leak Rate Comparison from PA-IR Leak Detection

Cell Design	Saehan	SKC	Quallion	Kokam	Electrovaya	LG
Mass (g)	43	63	96	159	161	241
Capacity (Ah)	2.1	3.3	3.4	8.3	7.4	9.4
Average Leak rate (mg/mo_DEC)	0.114	0.123	0.085	0.135	0.663	0.127
Average Leak rate (mg/mo_DEC) with T cycles	0.354	0.221	0.254	0.367	1.505	0.366
Leak rate/unit mass (mg/mo DEC/g)	0.002651	0.001952	0.000885	0.000849	0.004118	0.000527
ranking	5	4	3	2	6	1
Leak rate/unit mass (mg/mo DEC/g) w T cycles	0.008233	0.003508	0.002646	0.002308	0.009348	0.001519
ranking	5	4	3	2	6	1
Leak rate/unit Ah (mg/mo_DEC/Ah)	0.054286	0.037273	0.025000	0.016265	0.089595	0.013511
ranking	5	4	3	2	6	1
Leak rate/unit Ah (mg/mo_DEC/Ah) w T cycles	0.168571	0.066970	0.074706	0.044217	0.203378	0.038936
ranking	5	3	4	2	6	1

The LG cell design demonstrated the lowest leak rate per unit mass and per unit Ah, with ambient storage or with 24 thermal cycles between -40 and +54 °C. The Kokam design was next best followed closely by the Quallion in all categories except thermally cycled and compared by the Ah, where SKC comes in third.

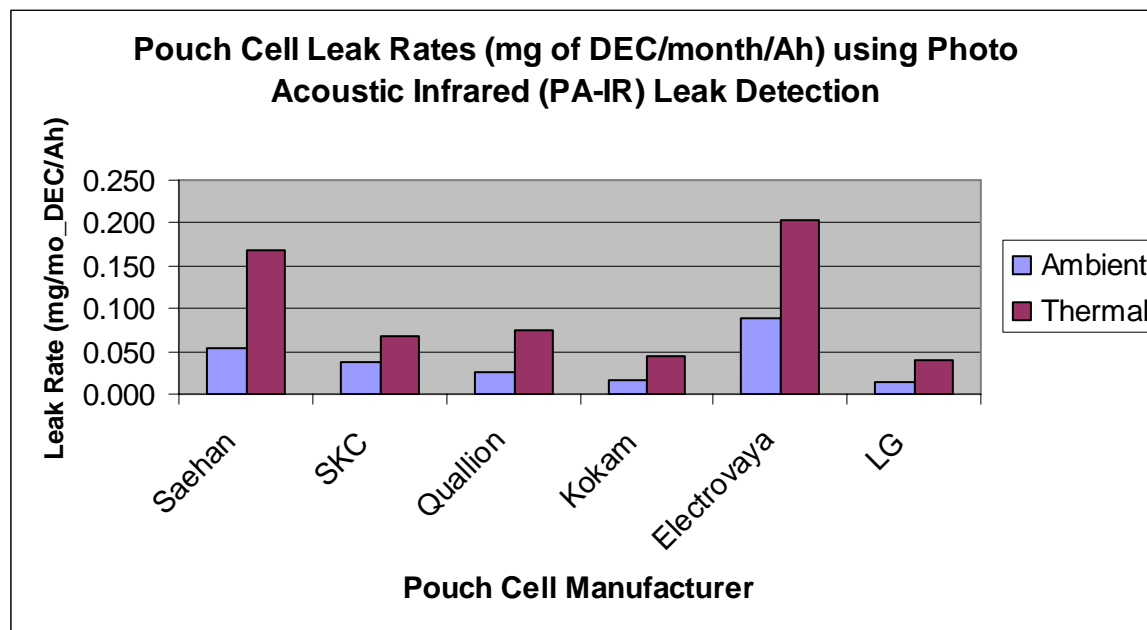


Figure 6.1-3. Comparison of Leak Rate per unit capacity of various cell designs with ambient storage and thermal cycle storage.



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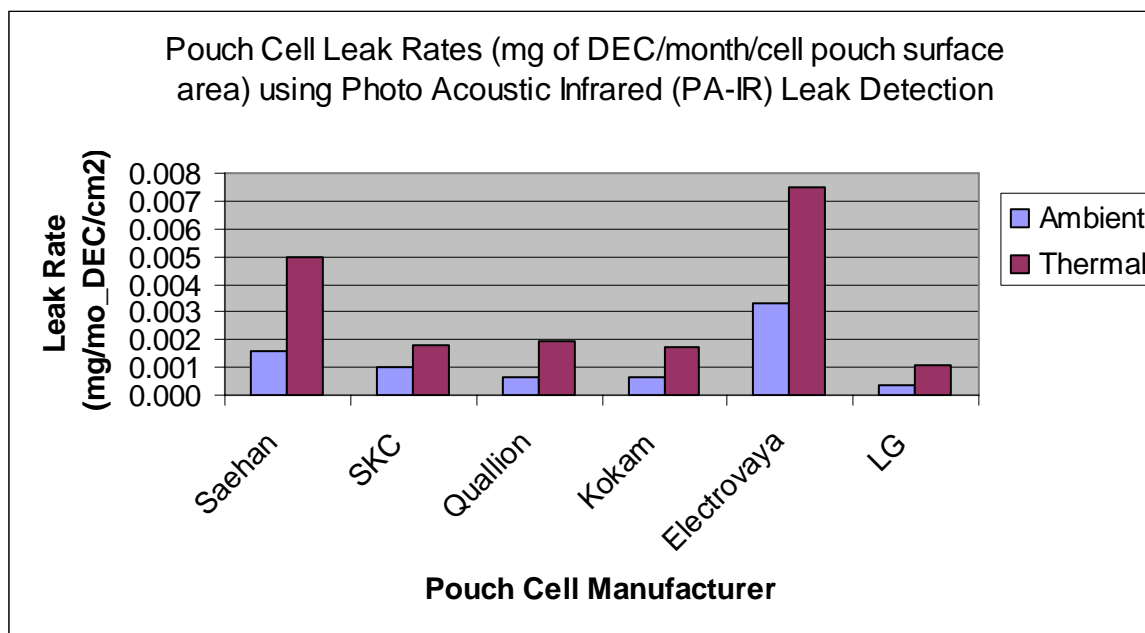


Figure 6.1-4. Comparison of Leak Rate per unit pouch surface area of various cell designs with ambient storage and thermal cycle storage.

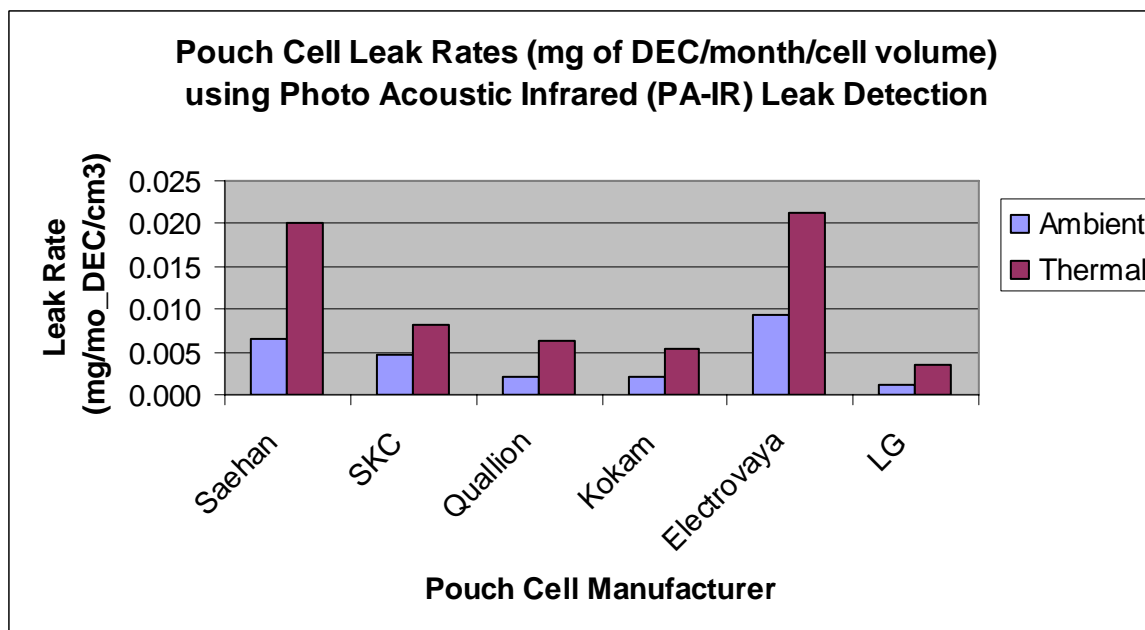


Figure 6.1-5. Comparison of Leak Rate per unit pouch cell volume of various cell designs with ambient storage and thermal cycle storage.

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In Figures 6.1-3 to 6.1-5, the comparisons of the pouch cell leak rates of DEC (the volatile component of the electrolyte solvent) are presented per unit capacity, pouch cell surface area, and cell volume. The order of best to worst does not change much (LG > Kokam > SKC, Quallion > Saehan > Electroveya) with each different metric.

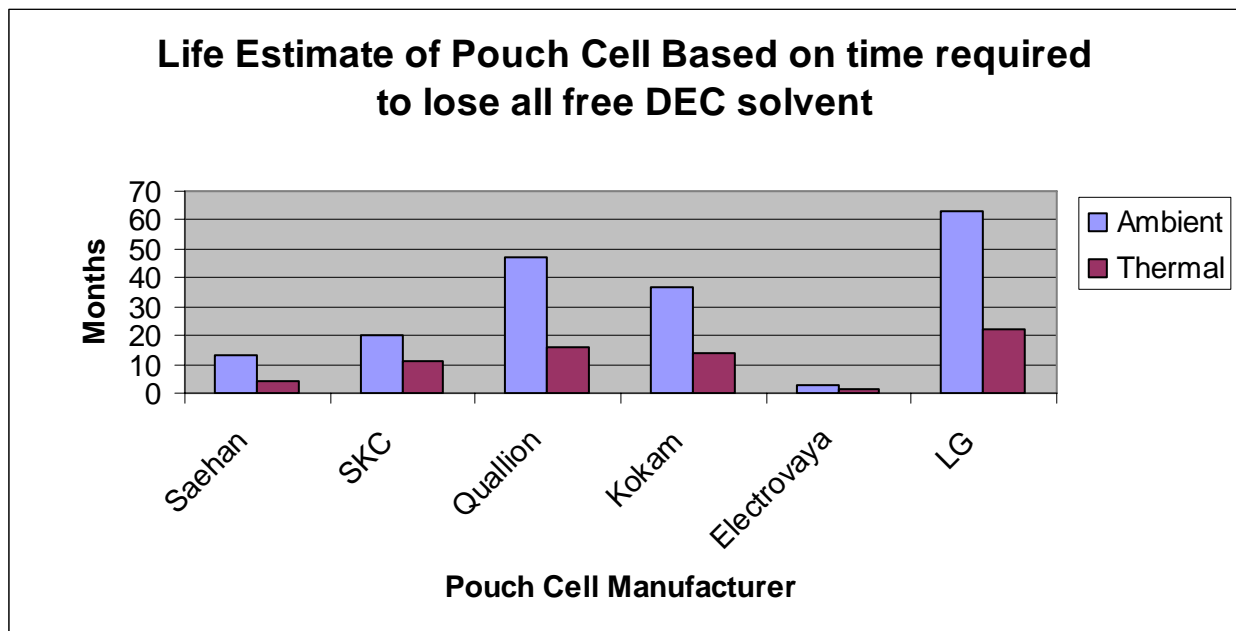


Figure 6.1-6. Comparison of the life estimate of various pouch cell designs with ambient and thermal cycle storage.

Assuming some quantities of free electrolyte for each cell designs based subjectively on DPA's performed, the team used the leak rates measured by PAIR to estimate how long it would take for all that quantity of electrolyte to exit the cell seals. It was assumed that the mass fraction of the volatile solvent was 50 percent of the electrolyte. Once the free electrolyte is gone, cell performance will measurably suffer.

The results (shown in Figure 6.1-6) are that the best cell design, LG, will last 63 and 22 months with ambient and thermal cycle storage, respectively. Note again, that these are based on estimated quantities of free electrolyte and that high rate cell designs requiring more electrolyte maybe be more sensitive to partial electrolyte loss.

Cross cut examinations of the tab to pouch seals of the LG, SKC, and Kokam cell designs were performed to elucidate similarities and differences. The LG and SKC designs are different from the Kokam in the following ways:

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- a) It appears that the LG and SKC pouch-to-tab seals are made with a 3-step process that stabilizes the location of the tabs relative to the pouch, melts the seal material, and then applies pressure to complete the seal. The die press used has sophisticated contours leaving marks (Figures 6.1-7 & 6.1-8) not seen on the other cell designs (Figures 5.1-8 & 6.1-1).
- b) The tabs were found to be centrally and symmetrically sealed between opposing pouch material layers.
- c) The multiple and distinct insulating layers exist in the inner side of pouch laminate material and those layers smoothly mix with the tab seal material. In Figure 6.1-9 (a & b), the tab seal and insulating layers of the Kokam pouch are not well integrated. While in Figure 6.1-10, they are for the LG cell.
- d) Edges (other than the tab seal edge) are sealed with a different sealer.
- e) Less excess separator material near the edge and corner seals and that separator material is unaffected by the sealing process.

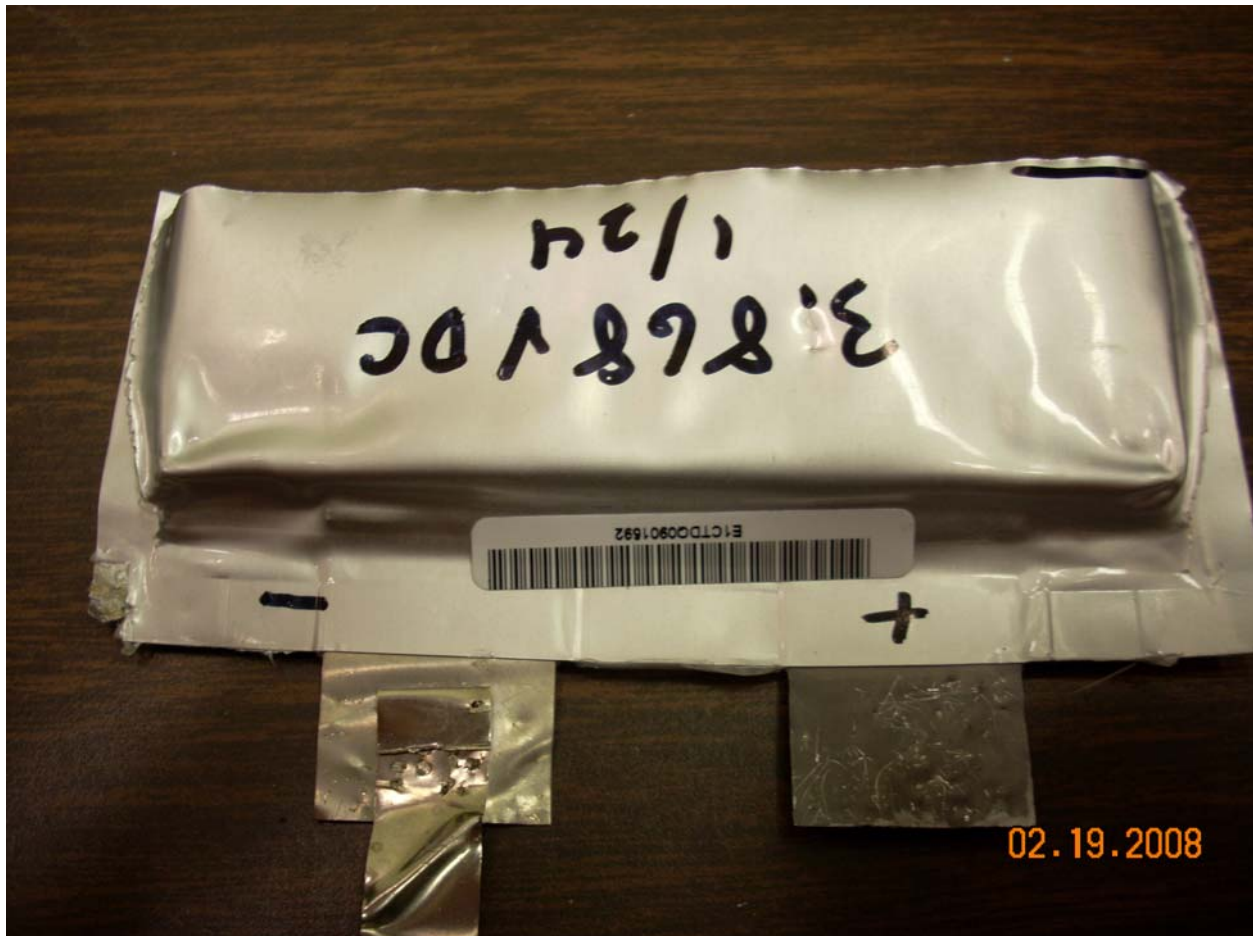


Figure 6.1-7. The tab-to-pouch and pouch-to-pouch seals of the LG cell design

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Figure 6.1-8. The tab-to-pouch and pouch-to-pouch seals of the SKC cell design

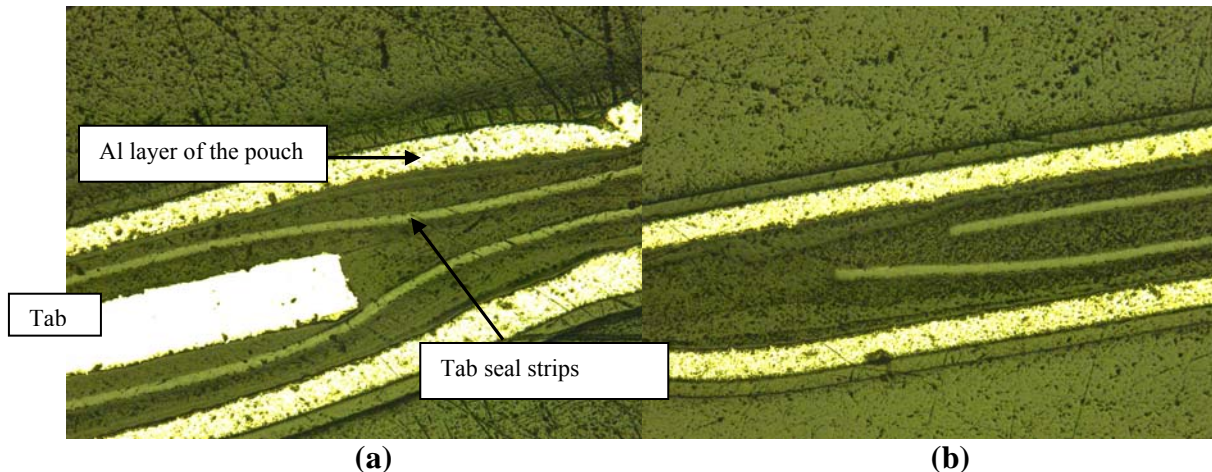


Figure 6.1-9. Cross-cuts of the tab-to-pouch seal (b) and tab seal material to pouch seal (a) at 300X magnification for the Kokam cell design. Note the distinct tab seal material not being well infused and integrated into the pouch insulation layers. Note the non uniform thickness of the pouch aluminum layer (b).

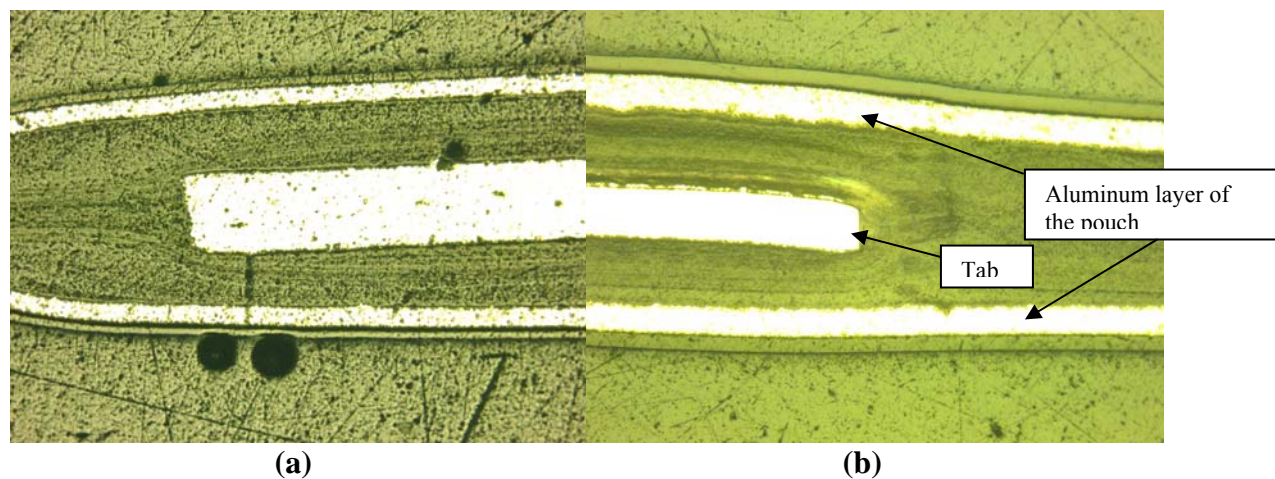



Figure 6.1-10. Cross-cuts of tab-to-pouch seals for LG (a) at 200X and for SKC (b) at 300X. Note how the tab seals are more integrated into the insulating layers of the pouch laminate for both of these designs than in Figure 6.1-9 for the Kokam design.

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Task II : Recommendations for Aerospace Applications of Pouch Cells

Characterization Data

SKC Polymer Cells

As part of formation (which may have already been done by the manufacturer, seven SKC gel polymer electrolytes cells were discharged initially at 20°C and -20°C at a nominal discharge rate of C/5. Also, in the last discharge cycle, the cell impedances were measured by DC current interrupt method. Table 6.1-3 summarizes the discharge data and the impedance values at 100 percent, 75 percent and 50 percent state of charge (SOC). The specific energies are impressive with over 160 Wh/kg, as may be expected from the pouch cell designs. Further, the impedance (of ~25 mOhms) is comparable to cells with liquid electrolyte even with a gel polymer electrolyte. Subsequent to this formation cycling, the cells were been further characterized for their rate capability from C/10 to 1.5C at different temperatures, i.e., 25, 0, -10, 20 and -30°C. Figure 6.1-11 shows the rate capability of these cells at 25°C and -20°C.

Table 6.1-3. Values of Discharge capacity, energy and impedance of seven SKC Polymer cells at C/5 at 25°C

Cell ID	Cell Weight (Grams)	Cell Weight (kg)	Initial Voltage	Initial Capacity (Ah)	Initial Watt-Hours	Initial Wh/kg	Calculated Impedance (mOhms) (100% SOC)	Calculated Impedance (mOhms) (75% SOC)	Calculated Impedance (mOhms) (50% SOC)
SKC01	78.56	0.0786	3.824	3.3940	12.825	163.25	27.30	30.81	36.95
SKC03	79.03	0.0790	3.826	3.3729	12.744	161.26	27.88	31.34	38.02
SKC04	78.68	0.0787	3.825	3.3783	12.764	162.22	28.08	31.18	37.24
SKC05	78.95	0.0790	3.826	3.3834	12.791	162.02	26.72	29.94	35.76
SKC06	78.67	0.0787	3.825	3.3878	12.797	162.67	29.03	32.62	38.81
SKC07	79.63	0.0796	3.820	3.3958	12.825	161.06	25.53	28.91	35.14
SKC08	79.05	0.0791	3.828	3.3873	12.821	162.19	22.52	28.83	29.82
Average	78.94	0.079	3.825	3.386	12.795	162.10	26.72	30.52	35.96



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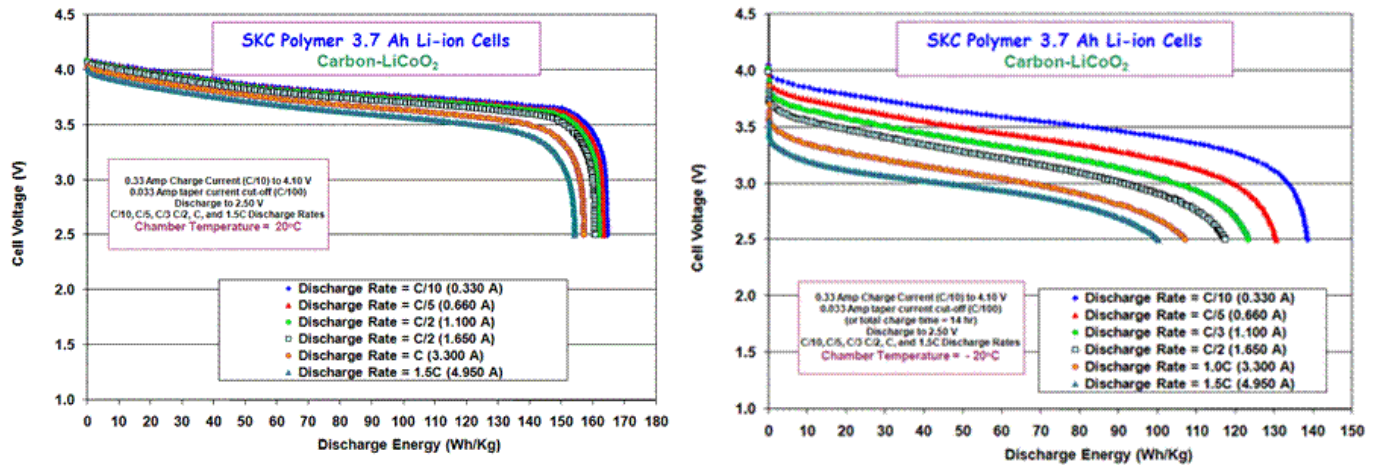



Figure 6.1-11. Rate capability of SKC polymer cells at 25°C and -20°C

As may be seen from the above figure, the cells have good rate capability combined with good low temperature performance, with over 100 Wh/kg at high discharge rates of C and 1.5C.

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Quallion Pouch Cells

As mentioned above, ten Quallion pouch cells of ~ 4 Ah were available for this study with three different electrolytes, one being the baseline and other two being low temperature electrolyte. These cells with three different electrolytes were studied to understand the extent of internal pressure build up that would breach the integrity of the cell. Table 6.1-4 shows the discharge capacities and impedance of these cells at 25°C.

Table 6.1-4. Values of Discharge capacity, energy and impedance of Quallion pouch cells with different electrolytes at C/5 and 25°C

Cell ID	Cell Weight (Grams)	Cell Weight (kg)	Initial Voltage	Initial Capacity (Ah)	Initial Watt-Hours	Initial Wh/kg	Calculated Impedance (mOhms) (100% SOC)	Calculated Impedance (mOhms) (80% SOC)	Calculated Impedance (mOhms) (60% SOC)	Electrolyte Type
QA05	79.18	0.0792	3.426	4.3847	16.009	202.19	29.98	39.52	30.44	ED-1
QA06	78.39	0.0784	3.446	4.3864	16.019	204.34	29.83	39.22	29.68	ED-1
QA07	79.11	0.0791	3.451	4.3714	15.951	201.63	30.98	40.74	33.88	ED-1
QA08	79.92	0.0799	3.703	4.3750	15.963	199.73	32.88	42.50	34.10	ED-1
QB04	78.47	0.0785	3.477	4.2974	15.626	199.14	35.86	45.93	37.16	ED-2
QB05	78.69	0.0787	3.461	4.5360	12.640	160.63	65.23	77.21	68.67	ED-2
QB06	79.28	0.0793	3.480	4.2537	15.477	195.22	35.48	47.46	37.92	ED-2
QB07	79.07	0.0791	3.483	4.2530	15.492	195.93	31.43	42.65	32.20	ED-2
QX010	80.31	0.0803	3.431	4.3436	15.818	196.96	33.88	44.10	34.49	Baseline Electrolyte
QX018	79.66	0.0797	3.4176	4.3172	15.712	197.24	34.56	45.93	35.78	Baseline Electrolyte
Average	79.21	0.08	3.48	4.25	15.47	195.30	36.01	46.53	37.43	

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Once again, the specific energies are impressive in the range of 200 Wh/kg, while the impedances are about 30 mOhms, comparable to the SKC polymer cells. As mentioned in the previous section, the higher specific energies may have been achieved with lower anode to cathode capacity ratios. These cells have been assessed for their performance at various low temperatures at different discharge rates. Figure 6.1-12 illustrates their relative abilities of these cells to operate at low temperatures of -20, -30, -40 and -50°C.

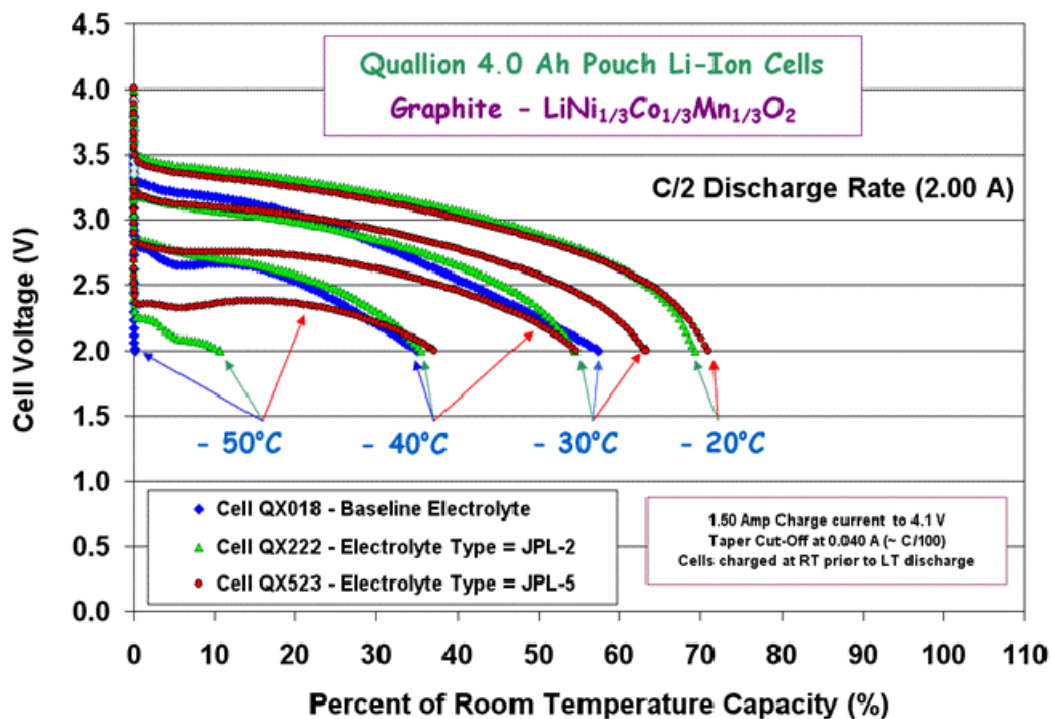


Figure 6.1-12. Rate capability of Quallion pouch cells with different liquid electrolytes at -20°C

As seen from the figure, the performance of the baseline electrolyte is fairly good, almost similar to JPL -3 (all-carbonate) formulations, but at -50°C, the baseline electrolyte is non-operational. The JPL-5 electrolyte, which is an ester blend, performed the best at low temperatures, with comparable performance at room temperature.

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LTC Pouch Li-ion cells

The pouch Li-ion cells used for these studies were at least two years old and contain meso-carbon micro-beat (MCMB) anode and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode with a conventional liquid electrolytes. Figure 6.1-13 shows the specific energies of these cells at different discharge rates, both at 20°C and -20°C.

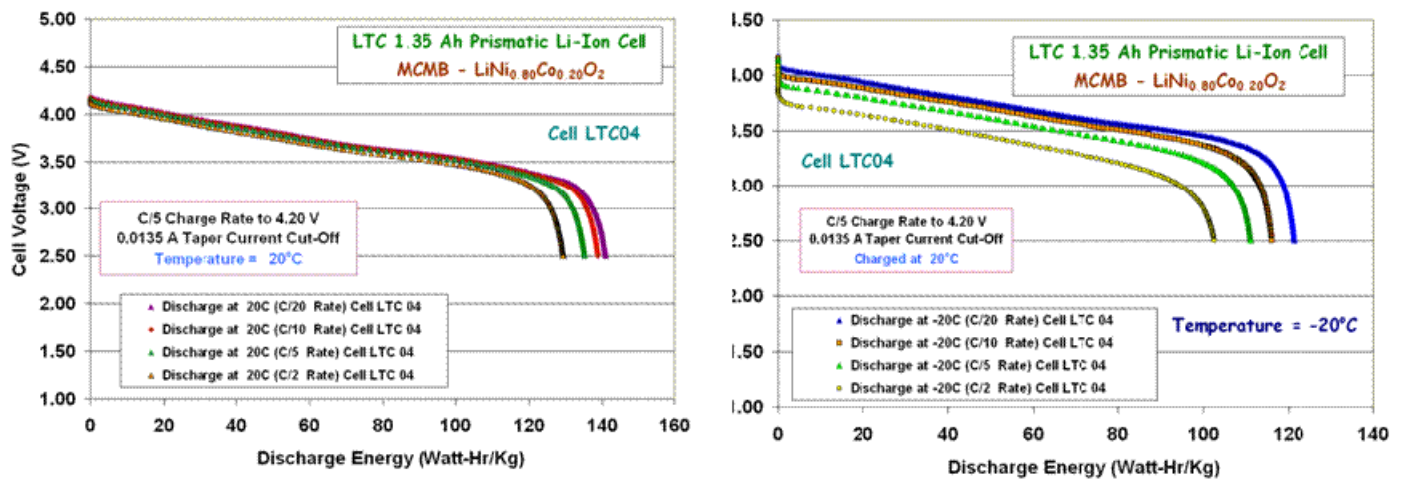


Figure 6.1-13. Rate capability of Quallion pouch cells with different liquid electrolytes at 20°C and -20°C

As seen in the figure, the cells have modest specific energies in the range of 140 Wh/kg at C/20, but lose almost 10 percent of their capacity at C/2. Their low temperature performance is also decent with about 70 percent realized at a rate of C/5 at -20°C, much like our MER cells with gen-1 electrolyte.

Compact Power Li-ion gel polymer Pouch cells

As mentioned above, these cells contain spinel manganese oxide, LiMn_2O_4 as cathode and a gel polymer electrolyte, with a conventional liquid electrolyte as plasticizer. These have a capacity of ~ 7 Ah and were at least four years old. In fact, they have been well tested during this period, as shown in Figure 6.1-14.

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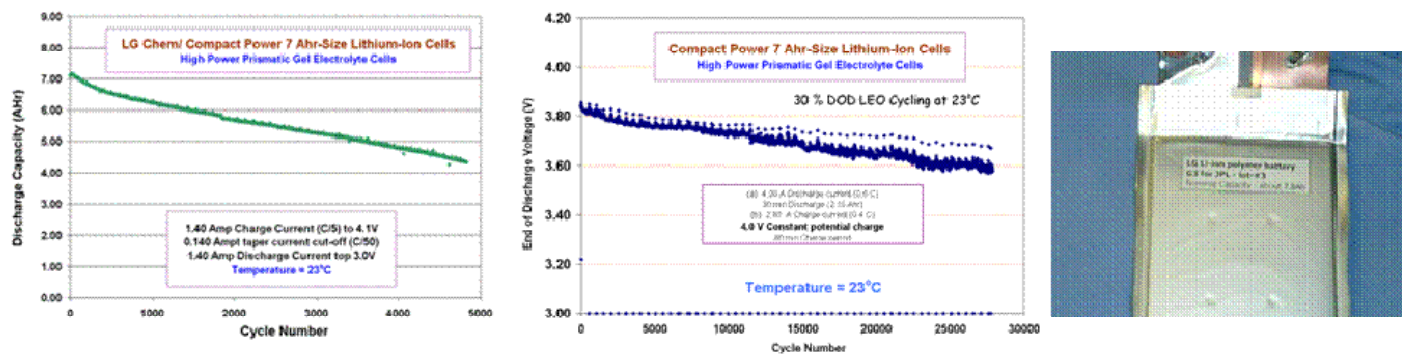


Figure 6.1-14. Cycle life of Compact Power Li-Ion cells with gel polymer electrolyte

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The cells display impressive cycling characteristics, both under deep discharge (100 percent DOD) cycling (almost 5000 cycles to > 50 percent capacity) and partial-DOD cycling as in LEO regime (about 29000 cycles at 30 percent DOD). The long cycle life of these cells implies that the pressure developed within the cell, even when charged to 4.1 V is low enough to be contained within the pouch, or ii) the pouch sealing is adequately strong. Furthermore, these pouch cells showed impressive low temperature performance even at -60°C , when the liquid electrolyte (plasticizer) was replaced with various JPL electrolytes (Figure 6.1-15). In any case, this is encouraging and pointing to a likely tolerance to hard vacuum environment as well.

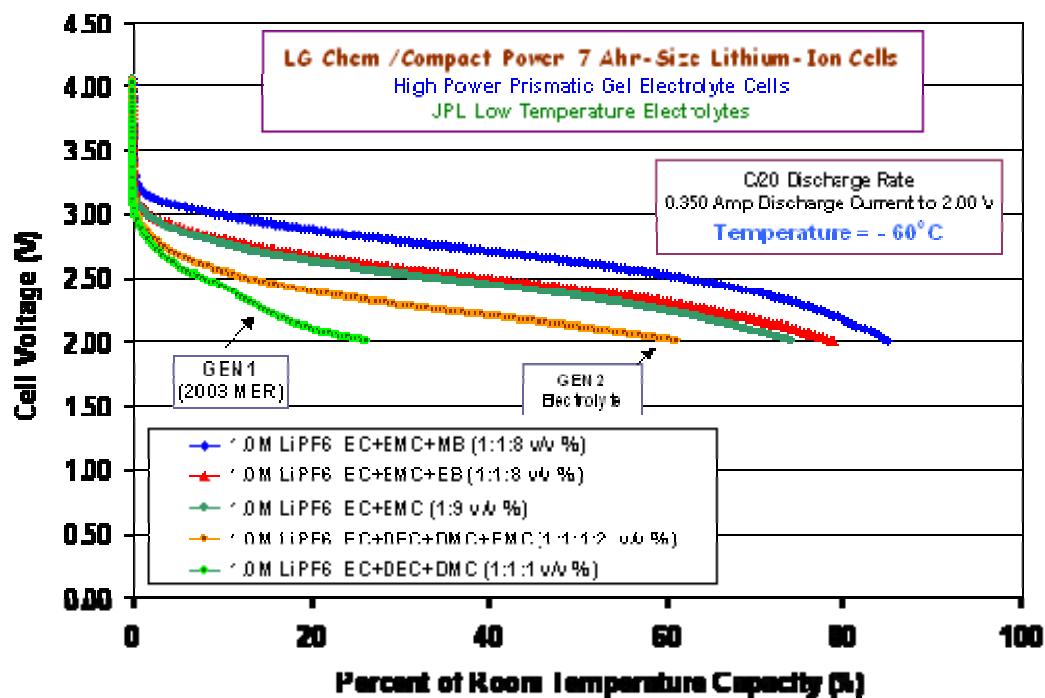


Figure 6.1-15. Low temperature performance of Compact power pouch cells with different JPL electrolytes

High Temperature Cycling

To accelerate the failure of the polymer cells upon cycling, the cells were cycled at 60°C, using the same charge voltage (4.1 v, with a taper). Figure 6.1-16 shows the performance of Quallion cells with baseline and low temperature electrolyte, LTC cell and SKC cell.

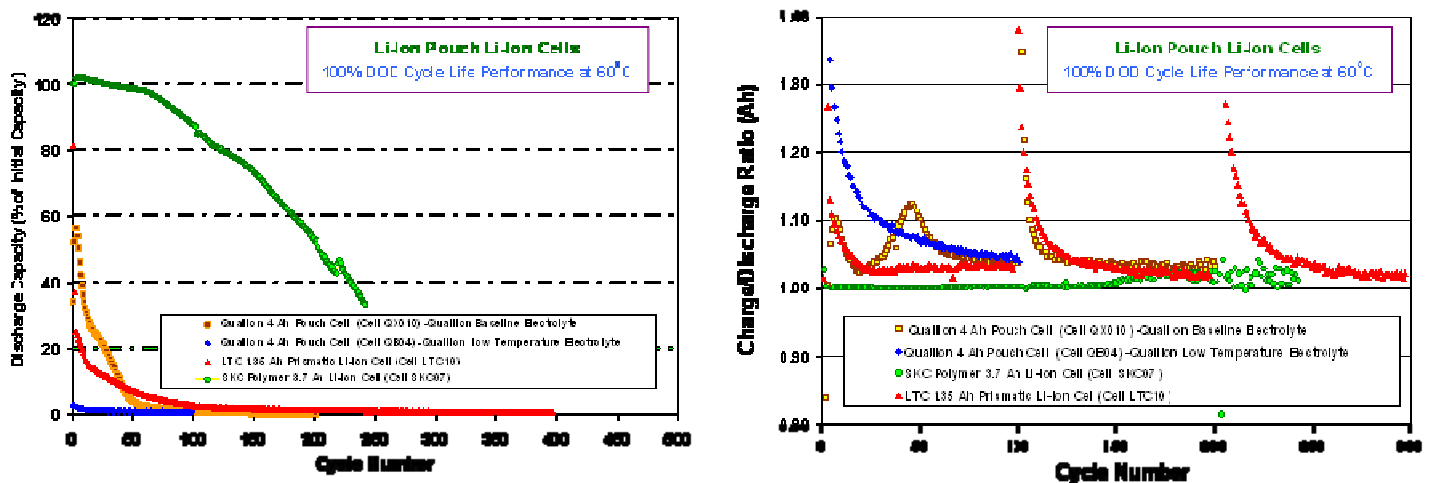


Figure 6.1-16. High temperature (60°C) cycling of various pouch cells showing rapid capacity fade, accompanied by high charge to discharge capacity ratios.

Interestingly, both Quallion cells failed early, with the low temperature electrolyte failing right away, while the baseline electrolyte cell surviving barely 20-30 cycles. The LTC cell lost the entire capacity within 50 cells. The SKC cell, on the hand, showed good resilience, showing about 50 percent capacity after 200 cycles. This amount of fade may be expected even in a conventional metal-contained Li-ion cell. The cell hasn't exhibited any rupture which is very encouraging. Among these cells, the cells that failed have unusually high charge to discharge capacity ratios, which suggests that there was considerable amount of electrolyte oxidation, probably internal pressure build up as well. The differences observed here among these four cells may be attributed to the following factors:

- Nature of electrolyte, especially solvent, which undergoes oxidative degradation during high temperature cycling.
- Amount of electrolyte (normalized to the volume of the cell), which could be higher for the Quallion cells, based on higher energy densities.
- Type of cathode material: Quallion cells, believed to have, continued NMC (0.33:0.33:0.33 Ni, Mn and Co) cathodes, while SKC cells contain lithiated cobalt oxide
- Type of electrolyte (either gel or liquid) and finally the
- Pouch seal design

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It is difficult to attribute the observed trend to any single factor and further studies are required to gain an understanding on the relative impact of these parameters.

6.1.2.2 High Voltage Risk Assessment: Limitations of Internal Protective Devices in High-Voltage/High-Capacity Batteries Using Li-Ion Cylindrical Commercial Cells

The following tests were initiated and carried out as part of the study to understand the failure causes and mechanisms in multi-cell series (string) or parallel (bank) modules.


1. Single Cell PTC tests to determine the PTC characteristics and limitations (Appendix G)
2. CID header only tests with various voltage limits (Appendix H)
3. CID single cell overcharge tests with various voltage limits (Appendix I)
4. External short and overcharge tests on cells in Parallel or Series configurations (Appendix J)
5. Research on a diode for the diode protection scheme (Appendix K)

Each test is described briefly and a summary of the test results is provided.

Single cell tests were performed to understand the withstanding (threshold) voltage limitations of the PTC from the point at which electrolyte leakage odor could be detected to a catastrophic ignition. Cell headers were removed from the cells and subjected to high voltages in the presence of electrolyte vapors. This test provided data on incidences of arcing when the two discs comprising the CID move apart to cause loss of electrical connectivity. A third set of tests was performed on single cells using the same method described above. A fourth set of tests included testing cells in series or in parallel under external short circuit and overcharge conditions. For this test, the number of cells in series or in parallel was varied and for the overcharge tests, the charge current as well as the voltage limits were changed. Finally, market research was carried out to identify a robust diode that would provide protection against a catastrophic failure under high voltage external short conditions.

Results of the tests indicated that the PTC used in cells varied by cell manufacturer. The robustness of the PTC also varies by cell manufacturer. Interestingly, the PTC tests on cells from different vendors indicated that the PTCs generate 3.2 to 3.5 W of heat in the tripped state, regardless of the load (or current) or the voltages applied to trip it. The PTC resistance for the tripped cells was observed to have been doubled.

Similarly, the designs of the CID were very varied and although the pressures required to cause a separation of the discs were in a similar range, the CIDs had different withstanding voltages with respect to the arcing phenomenon. Within the limited repetitions of the CID tests with the cell headers, arcing occurred about 30 percent of the time. When the same test was carried out with a full cell (again with very limited repetitions), no arcing was observed. However, incidences of discoloration of the CID discs were observed. All results are contained in Appendix H of Volume II.

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The string (cells in series) level tests indicated that ignition of the PTC under external short conditions in high voltage strings can occur leading to a catastrophic failure with cells venting with electrolyte leakage. No such events occurred when the cells were arranged in parallel in a single bank and externally shorted. Cell strings up to 4 cells in series, under overcharge condition displayed activation of cell CID with no catastrophic occurrence. However, a 14-cell string under the same conditions displayed violent cell venting and thermal runaway. During cell bank (parallel configuration) overcharge, catastrophic thermal runaway condition was dependent on the charge current as well as power supply voltage limits, independent of the bank size. It was also noted that if the PTC of the cells were compromised even in the slightest possible manner (slight increase in resistance), the results were catastrophic. All tests with the cell strings and banks were carried out with the cells arranged in a single row (fence post type). Under overcharge conditions, the cells in the bank that had compromised PTCs, went into a thermal runaway condition while the fresh cells with uncompromised PTCs did not.

Although the CID can arc in some of the cell designs, this may not always occur in actual cells due to the dampening or buffering of the reaction in the presence of electrolyte. At high voltages under overcharge conditions, excessive gas is produced due to the addition of lithium carbonate and at some point when the pressure of the gas is high enough to cause a deflection of the CID disc, the presence of free liquid electrolyte in the cell could cause the hot liquid electrolyte and its hot vapors to spurt into the CID reducing the arcing effect. The spurting of the hot liquid electrolyte and its vapors could result in a catastrophic event if the PTC or the cell header portion is heated due to the continued overcharge condition. At the same time, the heat in the cell could cause melting down of the cell seals and cause shorting in the cell. The presence of electrolyte and traces of seal material on the CID disc were confirmed by EDS.

6.1.2.3 Definition of Safe Limits for Charging Li-Ion Cells

Lithium plating is a result of relatively slow kinetics for Li intercalation (into graphite) compared to Li deposition and is thus governed by all the conditions that affect the interfacial properties at the anode. More specifically, it is dependent on the: i) nature of electrolyte, ii) nature of anode composite electrode, and iii) cathode to anode capacity ratio. Generally, Li-ion cell designs are cathode limited. However, if anode is not sufficiently in excess, it may be polarized heavily during charge, which will drive the anode to potentials conducive to Li plating. Further, the cathode to anode ratio may change upon cycling/storage, due to a relatively faster degradation of the anode capacity. Our studies confirm these dependencies as shown below.

Effect of electrolyte

A low temperature electrolyte provides suitable interfacial conditions that would facilitate Li intercalation and hence mitigate the problem of Li plating. Figure 6.1-17 and 6.1-18 give examples of two electrolytes: i) Ethylene carbonate-rich formulation (in Figure 6.1-17), and ii) a low EC-content blended electrolyte, good for low temperature operations.

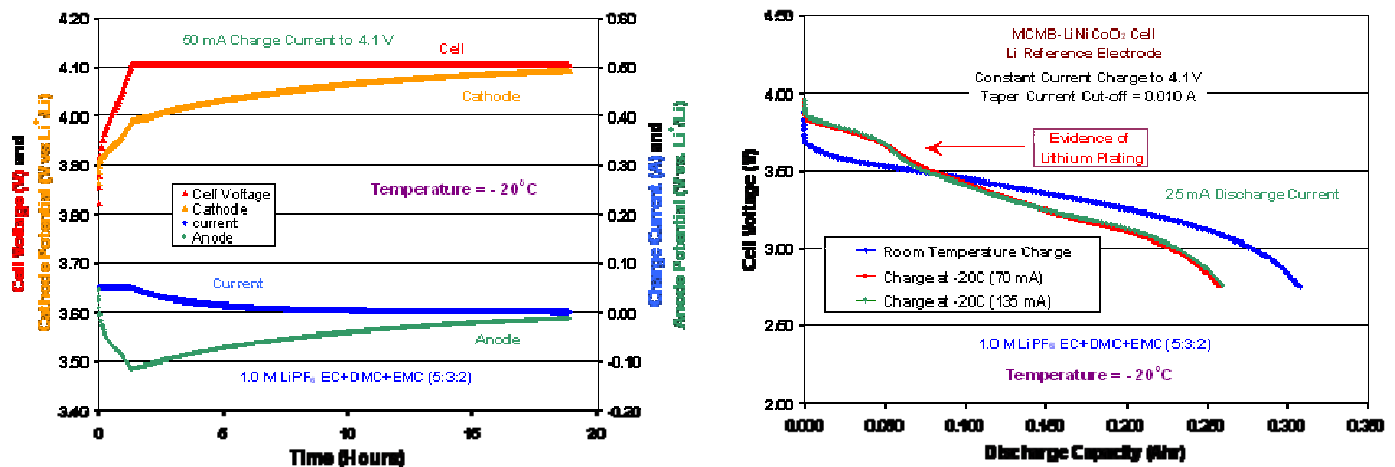


Figure 6.1-17. Cathode and anode potentials during charge at -20°C and cell discharge curves during subsequent discharge, showing Li plating in high EC electrolyte

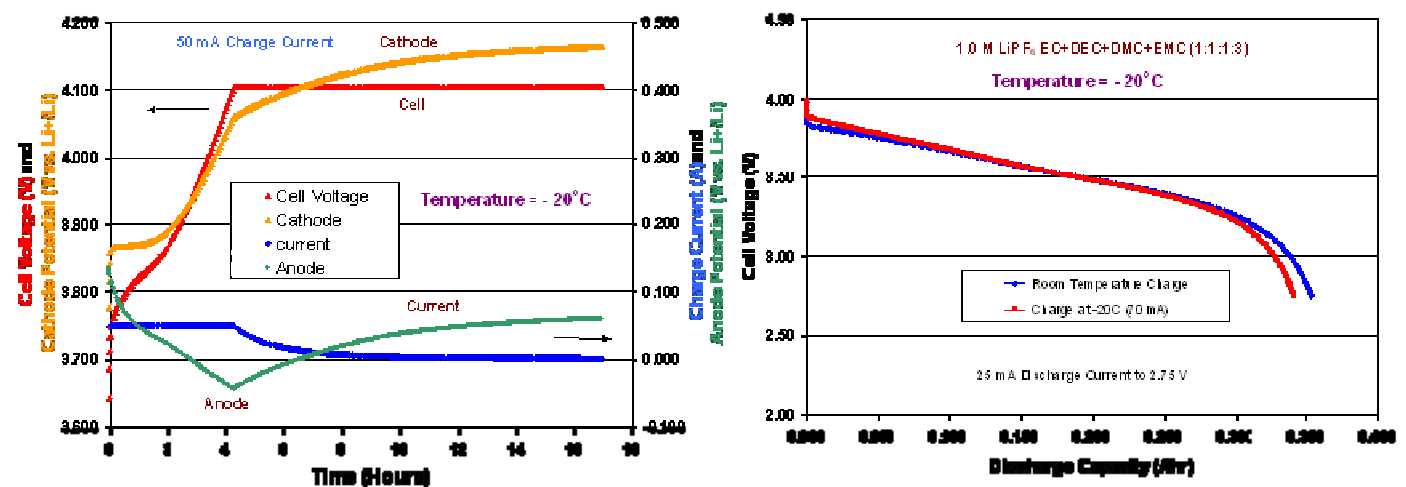



Figure 6.1-18. Cathode and anode potentials during charge at -20°C and cell discharge curves during subsequent discharge, showing no evidence of Li plating in one of JPL's low temperature electrolytes

As may be seen from the above figures, the low temperature electrolyte provides suitable interface for (good) Li intercalation kinetics and less so for Li plating. This is further substantiated by the Tafel polarization data, which show the relative kinetics at the individual

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electrodes, as shown in Figure 6.1-19.

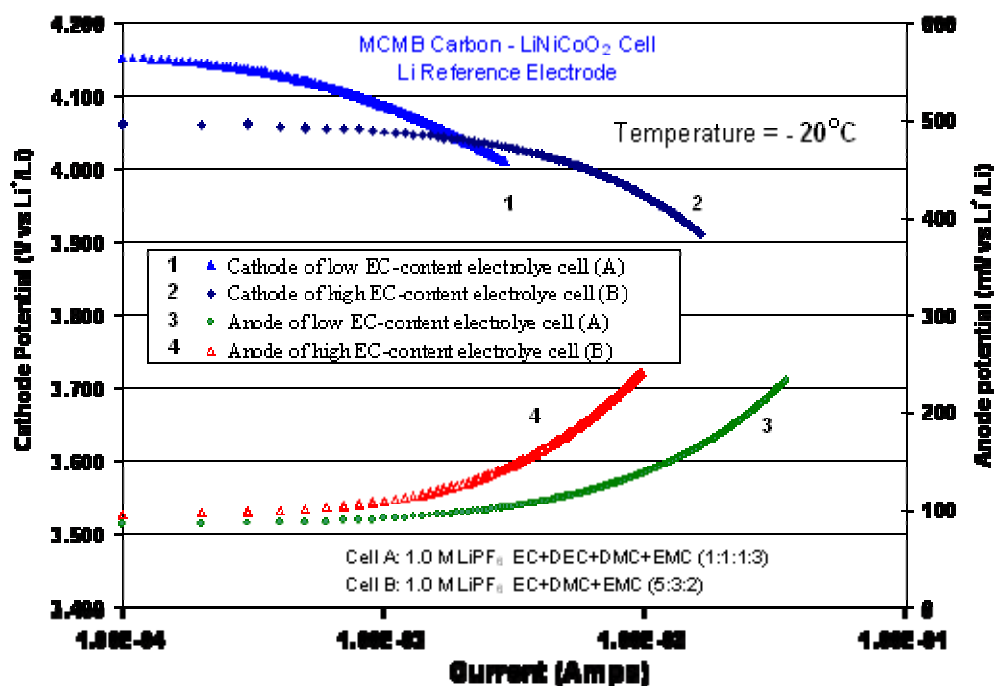


Figure 6.1-19. Tafel polarization curves of cathodes and anodes at -20°C in contact with the EC-rich and low-EC (low temperature) electrolytes

It is clear from the above figure that the anode kinetics are slower compared to the cathode kinetics in the EC-rich electrolyte, which would have subjected the anode to a heavier polarization and subsequently to lithium plating, as observed in Figure 6.1-17.

Effect of anode to cathode ratio

High anode to cathode (capacities) ratio will minimize polarization at the anode during charge, which in turn precludes Li plating on the anode. Figures 6.1-20 and 6.1-21 provide a comparison of the two prototypes, which differ more prominently in the anode to cathode ratio among other design variations.

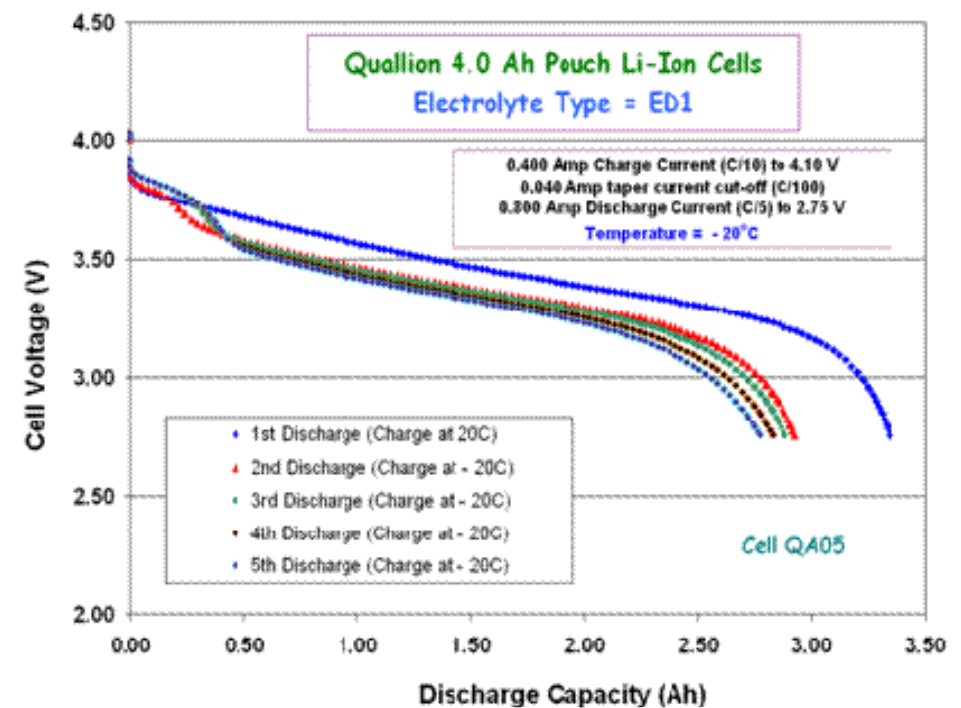
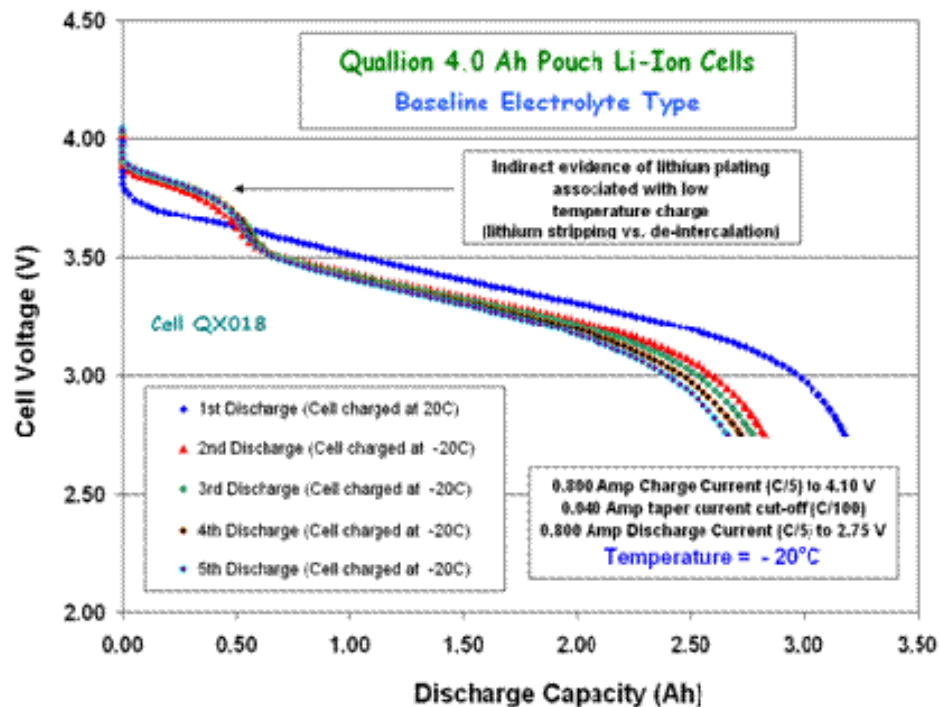


Figure 6.1-20. Discharge curves for Quallion pouch cells with baseline and low temperature electrolytes, following a charge at -20°C, showing strong tendency of Li plating

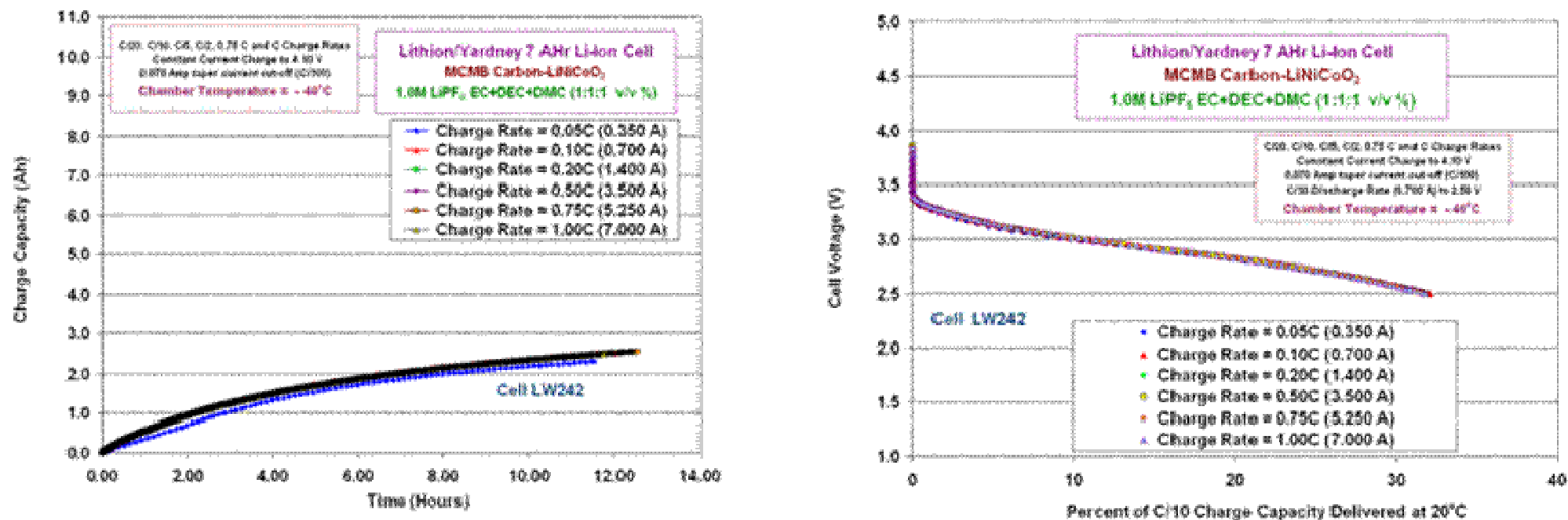


Figure 6.1-21. Charging of Yardney 7 Ah cells with JPL's gen-1 low temperature electrolytes at different charge rates at -40°C and subsequent discharge curves showing no evidence of Li plating.

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The cells shown in Figure 6.1-20 were fabricated by Quallion in pouch configuration and have capacities of 4 Ah. Based on their specific energies of about 190 Wh/kg, it can be inferred that these cells have a lower anode to cathode ratios. This may be a significant factor behind the tendency towards lithium plating at -20°C , with baseline as well as with low temperature electrolytes. The cells shown in Figure 6.1-21, made by Yardney, on the other hand have higher anode to cathode ratio inferred from their modest specific energies and are immune to lithium plating even at -40°C .

Intercalation vs. Plating Kinetics

To express the effect of kinetics quantitatively, the team estimated the currents going towards Li plating and Li intercalation at a given potential. These estimates were made with the assumption that both Li processes are in the Tafel mode at the selected voltages. The value of reversible potential for Li intercalation used for this calculation is 85 mV vs Li, while the potential for Li plating: 0 V vs. Li. As seen in Figure 6.1-22, proportion of plating current starts climbing up from ~ 2 percent to > 10 percent, if the ratio of exchange currents for intercalation to plating goes below 20. In other words, if the intercalation kinetics are only 20 times faster than plating (which is the case at low temperatures), lithium plating current starts being substantial.

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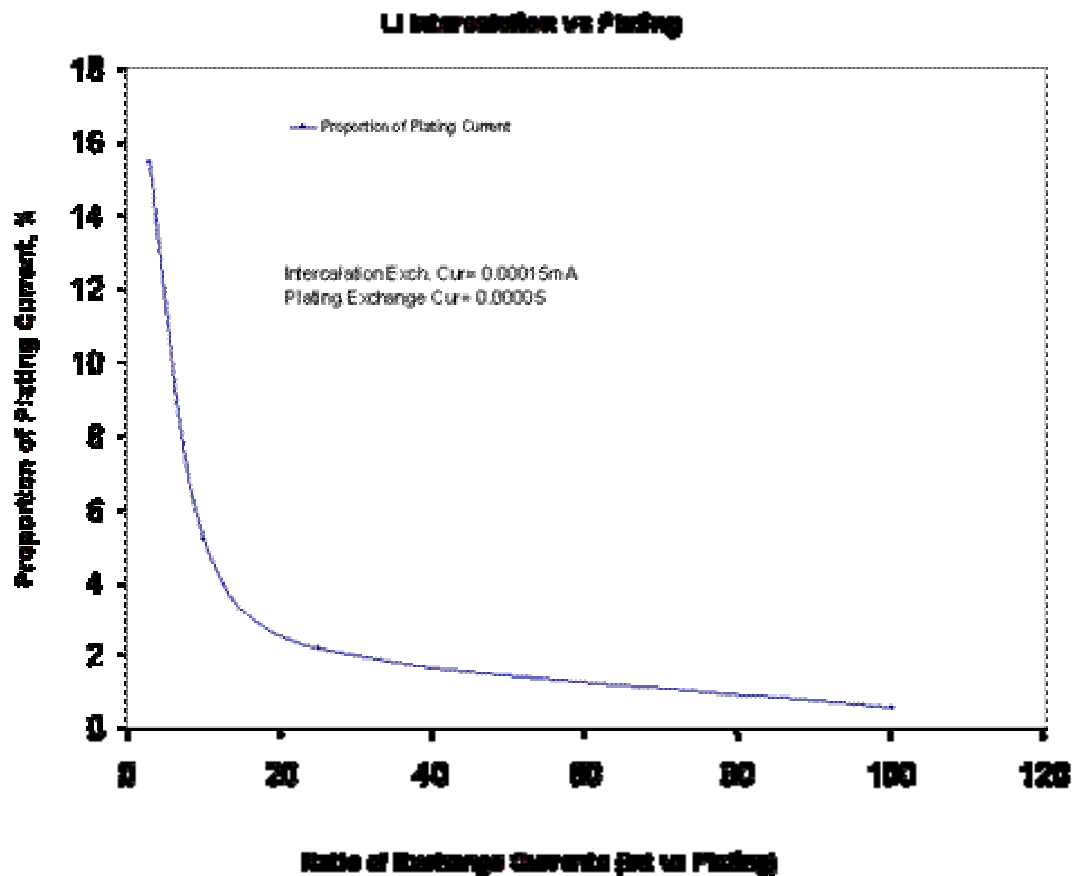



Figure 6.1-22. Proportion of plating current as a function of the relative kinetics for plating and intercalation

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Summary of the Test Data

Table 6.1-5 summarizes the findings from different prototype cells tested in this program. It lists the acceptable (without Li plating) charge rates (in terms of C rate) of these different cells, at different temperatures.


Table 6.1-5. Demonstrated Li plating as a function of charge rate and temperature

Temperature	Charge rate	Yardney	A123 (COTS)	Quallion baseline (18650-	Quallion-ED1	Quallion-ED2	SKC	SAFT (EC+EMC)
	Charge Voltage	4.1 V	3.6 V	4.2	4.1	4.1	4.2	4.1
0	C/10	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating
	C/5	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating
	C/2	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating
	C	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating
-10	C/10	No Plating	No Plating	No Plating	No Plating	NA	No Plating	No Plating
	C/5	No Plating	No Plating	No Plating	No Plating	NA	No Plating	No Plating
	C/2	No Plating	No Plating	No Plating	No Plating	NA	No Plating	No Plating
	C	No Plating	Possibly	No Plating	No Plating	NA	No Plating	No Plating
-20	C/10	No Plating	No Plating	No Plating	Plating	Mild	Mild	No Plating
	C/5	No Plating	No Plating	No Plating	Plating	Plating	Mild	No Plating
	C/2	No Plating	Plating	Plating	Mild	Plating	Mild	Mild
	C	No Plating	Plating	Plating	Low capacity	Mild	Mild	Mild
-30	C/10	No Plating	Possibly	Plating	Low capacity	NA	Mild	Plating
	C/5	No Plating	Plating	Plating	Low capacity	NA	Mild	Plating
	C/2	No Plating	Plating	Plating	Low capacity	NA	Mild	Plating
	C	No Plating	Plating	Plating	Low capacity	NA	Mild	Plating
-40	C/10	No Plating	Low capacity	Negligible Ah	Negligible Ah	Negligible Ah	Possibly	Low capacity
	C/5	No Plating	Low capacity	Negligible Ah	Negligible Ah	Negligible Ah	Possibly	Low capacity
	C/2	No Plating	Low capacity	Negligible Ah	Negligible Ah	Negligible Ah	Possibly	Low capacity
	C	No Plating	Low capacity	Negligible Ah	Negligible Ah	Negligible Ah	Possibly	Low capacity

As seen from the above table, the propensity for Li plating as a function of charge rate and temperature varies significantly from one manufacturer to another. These variations may be related to the difference in materials, electrode and electrolytes, and in the cell designs, more importantly the amount of anode reserve.

Yardney 7 Ah Cells

As mentioned previously, a number of 7 Ah Li-ion manufactured by Yardney Technical Products were subjected to charge characterization testing at a number of temperatures (i.e., 20, 10, 0, -10, -20, -30, and -40°C) and using a number of charge rates (C/20, C/10, C/5, C/2, C/1.33, C/1.0). As shown in Table 6.1-6, when the cells were evaluated at 20°C, comparable capacity can be obtained in all cases, regardless of charge rate. This is due to the charging methodology consisting of implementing a constant current-constant

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potential (CC-CV) protocol, which allows the current to taper to a fixed value (i.e., C/50, or 0.140A) in the constant potential mode (e.g., 4.10V). Although the final charge capacity is comparable regardless of charge rate, proportionately more charge time is spent in the constant potential mode when high inrush charge currents are used, and lower watt-hour efficiencies are observed due to increased polarization. These differences are illustrated in Figures 6.1-23 and 6.1-24, in which the charge characteristics are displayed for one of the cells at 20°C using C/5 and C charge rates, respectively. As shown in Figure 6.1-23 when a C/5 charge rate is used the cell is in the constant current mode for 5.48 hours of the total 6.54 hour charge time, or ~ 85% of the total charge time. In addition, 7.697 Ah is charge capacity is accepted by the cell in the constant current mode, representing 95.6% of the total charge capacity.

Table 6.1-6. Summary of the charge characteristics of a Yardney 7 Ah cell at 20°C.

			Cell LW 242 1.0 M LiPF6 EC+DEC+DMC (1:1:1 v/v %)						
Temperature	Charge Rate	Discharge Current (A)	Charge Capacity (Ah)	Charge Time (Hours)	Percent C/10 Capacity	Percent C/10 Capacity at 20°C	Charge Watt-Hr (Wh)	Discharge Watt-Hr (Wh)	Watt Hour Efficiency (%)
20°C	0.05C	0.350	8.0568	23.3474	100.00	100.00	29.5035	28.9212	98.03
	0.10C	0.700	8.0523	12.0724	99.94	99.94	29.5767	28.9385	97.84
	0.20C	1.400	8.0533	6.5373	99.96	99.96	29.7489	28.9385	97.28
	0.50C	3.500	8.0492	3.3486	99.91	99.91	30.1778	28.9183	95.83
	0.75C	5.250	8.0396	2.6752	99.79	99.79	30.4619	28.8823	94.81
	1.00C	7.000	8.0324	2.4127	99.70	99.70	30.7237		

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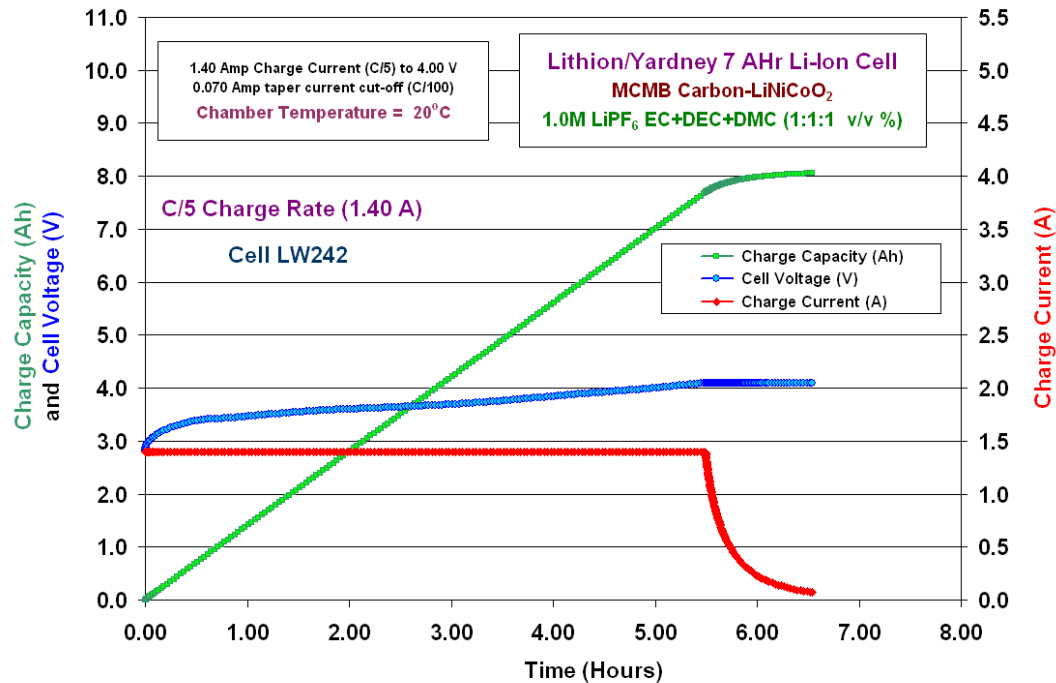


Figure 6.1-23. Charge characteristics of a Yardney 7 Ah cell at 20°C using a C/5 rate to 4.10V

In contrast, when using a C rate charge, the cell is in the constant current mode for 0.95 hours of the total 2.41 hour charge time, or ~39% of the total charge time. In addition, 7.697 Ah is charge capacity is accepted by the cell in the constant current mode, representing only 82.6% of the total charge capacity. Generally speaking, due to decreased cell resistance, high power cell designs typically have improved charge acceptance characteristics at high rates, and proportionately more charge capacity is obtained in the constant current mode as opposed to the constant potential mode. In contrast, cells with poor rate capability and/or cells that has impedance growth due to aging effects will typically have a larger proportion of the charge capacity being accepted during the constant potential mode.

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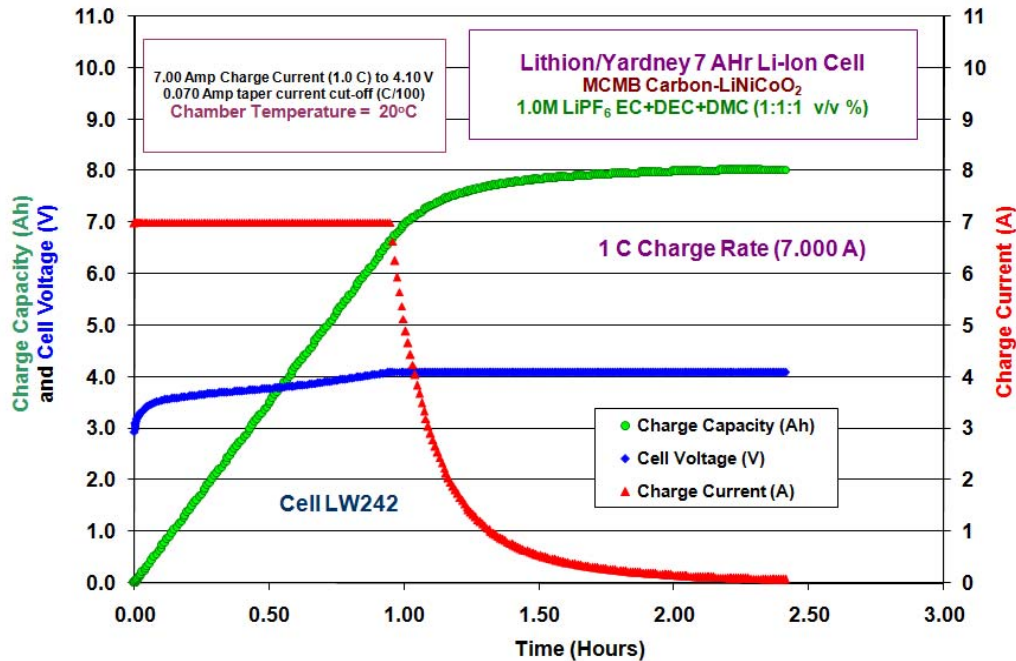


Figure 6.1-24. Charge characteristics of a Yardney 7 Ah cell at 20°C using a 1.0 C rate to 4.10V

This trend is also seen at lower temperatures, where more of the charge capacity is accepted during the constant potential mode rather than in the constant current mode, due to higher cell resistance. This results in correspondingly higher charge times to obtain “full” capacity. It should also be noted that lower charge capacities are obtained at lower temperatures, resulting in ~ 96 %, 90%, 83%, 75%, 61%, and 32% of the room temperature capacity for cells charged at 10°, 0°, -10°, -20°, -30°, and -40°, respectively. For example, when a cell was characterized at -20°C, as summarized in Table 6.1-7, only 74-75% of the room temperature capacity could be charged into the cell, regardless of charge rate employed. In addition, the charge time required to charge the cell is much longer, with the C rate charge taking over 7 hours to reach full capacity. This is illustrated in Figure 6.1-25, in which the charge characteristics of a 7 Ah cell are shown at -20°C using a C rate charge. As shown, only negligible charge capacity is accepted by the cell during the constant current mode, the cell being unable to support such high charge currents at these temperatures without being polarized above the set charge voltage of 4.10V. Thus, nearly all of the capacity is obtained during the constant potential mode, with over half of the capacity being accepted when the current has taper to values below 3A.

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Table 6.1-7. Summary of the charge characteristics of a Yardney 7 Ah cell at - 20°C.

			Cell LW 242 1.0 M LiPF ₆ EC+DEC+DMC (1:1:1 v/v %)						
Temperature	Charge Rate	Discharge Current (A)	Charge Capacity (Ah)	Charge Time (Hours)	Percent C/10 Capacity	Percent C/10 Capacity at 20°C	Charge Watt-Hr (Wh)	Discharge Watt-Hr (Wh)	Watt Hour Efficiency (%)
- 20°C	0.05C	0.350	6.0073	19.2501	100.00	74.56	22.9359	20.5176	89.46
	0.10C	0.700	6.0227	11.8156	100.26	74.75	23.3408	20.6344	88.40
	0.20C	1.400	6.0162	8.5451	100.15	74.67	23.7861	20.6448	86.79
	0.50C	3.500	6.0065	7.2249	99.99	74.55	24.4212	20.5940	84.33
	0.75C	5.250	5.9762	7.1198	99.48	74.18	24.4775	20.4916	83.72
	1.00C	7.000	5.9380	7.1191	98.85	73.70	24.3436	20.3758	83.70

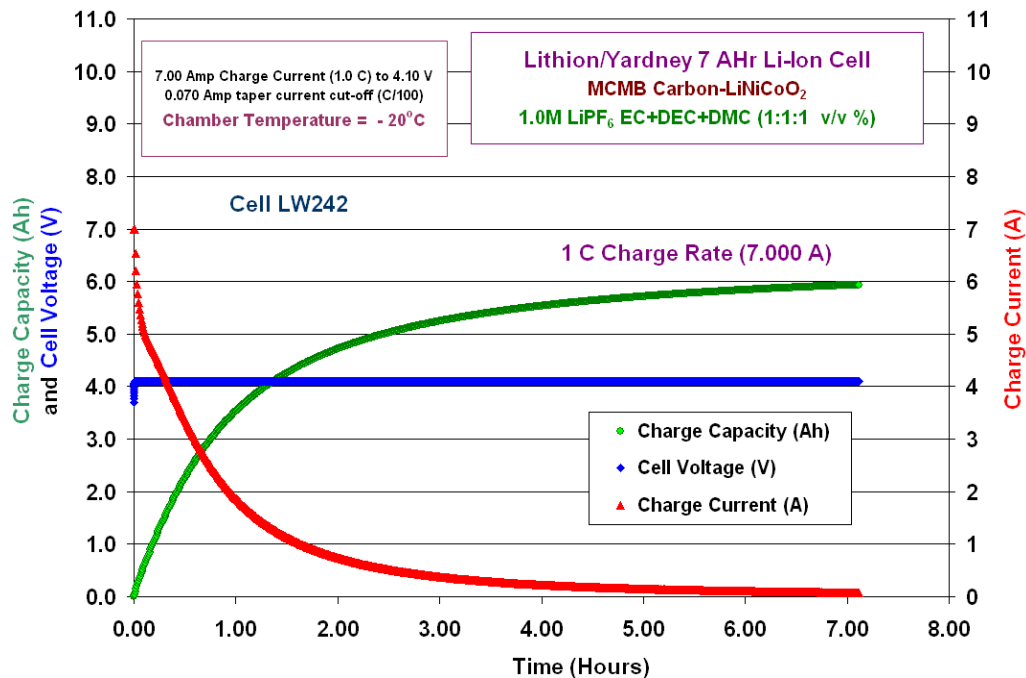


Figure 6.1-25. Charge characteristics of a Yardney 7 Ah cell at - 20°C using a 1.0 C rate to 4.10V

In terms of harmful lithium plating processes, the conditions that possess the greatest propensity for this occurring are when the charge current and the charge potential are the

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highest. Thus, in the case of the cell above, under the described conditions (C rate charge at -20°C), the likelihood of lithium plating is greatest at the very beginning of the charging process, i.e., when the charge current is the highest (e.g. above 3.0A) and the charge voltage is the highest (e.g., 4.10V). When the subsequent discharge profiles are observed following high rate charge at -20°C , as shown in Figure 6.1-26, no clear evidence of the corresponding lithium stripping phenomena is observed, indirectly suggesting that no significant lithium plating occurred or that any lithium that was plated at the higher currents intercalated into the graphitic anode over time when the cell was charging at the lower currents. For that matter, no evidence of lithium plating was observed (as ascertained by the subsequent discharge profiles) with the Yardney 7 Ah cells when characterized down to -40°C , and using charge rates of up to C rate. The summary of all the characterization tests performed on the baseline cell, which contained the ternary carbonate electrolyte (e.g., 1.0M LiPF_6 in EC+DEC+DMC (1:1:1 v/v %)), is shown in Table 6.1-8.

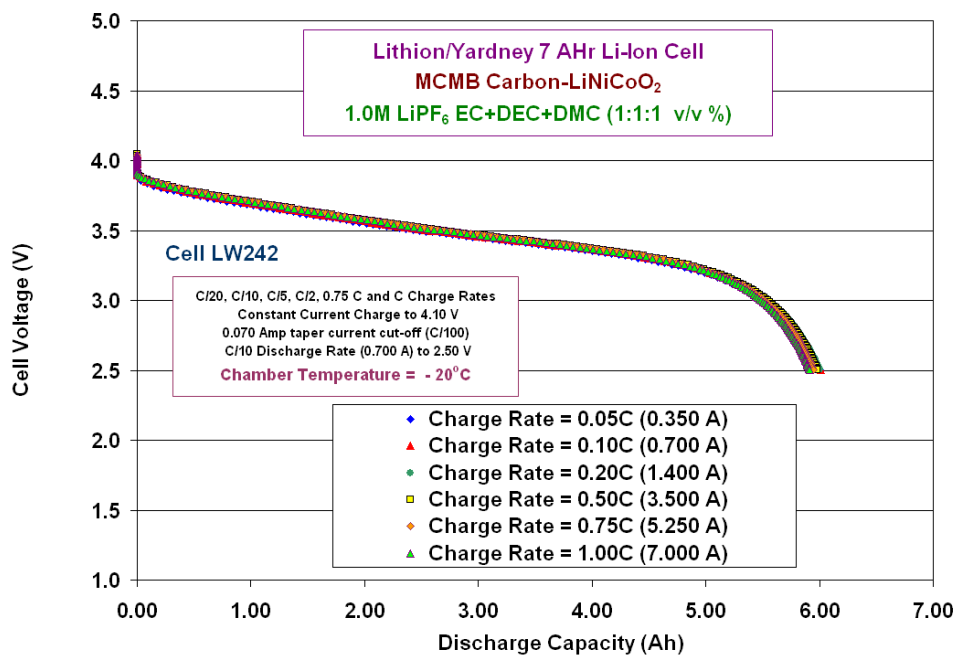


Figure 6.1-26. Discharge profiles of a 7 Ah cell after charging at various rates at low temperature (-20°C).

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Table 6.1-8 Summary of the charge characteristics of a Yardney 7 Ah cell, containing the baseline electrolyte 1.0M LiPF₆ in EC+DEC+DMC (1:1:1 v/v %) at various temperatures.

			Cell LW 242 1.0 M LiPF6 EC+DEC+DMC (1:1:1 v/v %)						
Temperature	Charge Rate	Discharge Current (A)	Charge Capacity (Ah)	Charge Time (Hours)	Percent C/10 Capacity	Percent C/10 Capacity at 20°C	Charge Watt-hr (Wh)	Discharge Watt-hr (Wh)	Watt Hour Efficiency (%)
20°C	0.05C	0.350	8.0568	23.3474	100.00	100.00	29.5035	28.9212	98.03
	0.10C	0.700	8.0523	12.0724	99.94	99.94	29.5767	28.9385	97.84
	0.20C	1.400	8.0533	6.5373	99.96	99.96	29.7489	28.9385	97.28
	0.50C	3.500	8.0492	3.3486	99.91	99.91	30.1778	28.9183	95.83
	0.75C	5.250	8.0396	2.6752	99.79	99.79	30.4619	28.8823	94.81
	1.00C	7.000	8.0324	2.4127	99.70	99.70	30.7237		
10°C	0.05C	0.350	7.7452	22.6225	100.00	96.13	28.5363	27.8336	97.54
	0.10C	0.700	7.7571	11.8935	100.15	96.28	28.7010	27.8456	97.02
	0.20C	1.400	7.7581	6.6386	100.17	96.29	28.9214	27.8356	96.25
	0.50C	3.500	7.7340	3.6653	99.86	95.99	29.3697	27.7578	94.51
	0.75C	5.250	7.7277	3.0941	99.77	95.92	29.7269	27.7027	93.19
	1.00C	7.000	7.7229	2.9136	99.71	95.85	30.0284		
0°C	0.05C	0.350	7.2584	21.4949	100.00	90.09	26.9728	25.9934	96.37
	0.10C	0.700	7.2665	11.5890	100.11	90.19	27.1700	26.0100	95.73
	0.20C	1.400	7.2649	6.8085	100.09	90.17	27.4519	25.9692	94.60
	0.50C	3.500	7.2390	4.2259	99.73	89.85	28.0234	25.8735	92.33
	0.75C	5.250	7.2338	3.8083	99.66	89.78	28.4049	25.8399	90.97
	1.00C	7.000	7.2195	3.6276	99.46	89.61	28.6730		
-10°C	0.05C	0.350	6.7039	20.3658	100.00	83.21	25.1701	23.7137	94.21
	0.10C	0.700	6.7180	11.5154	100.21	83.38	25.4718	23.7535	93.25
	0.20C	1.400	6.7108	7.3188	100.10	83.29	25.8389	23.7115	91.77
	0.50C	3.500	6.6941	5.2590	99.85	83.09	26.5356	23.6379	89.08
	0.75C	5.250	6.6737	4.9619	99.55	82.83	26.8405	23.5484	87.73
	1.00C	7.000	6.6562	4.9253	99.29	82.62	27.0337		
-20°C	0.05C	0.350	6.0073	19.2501	100.00	74.56	22.9359	20.5176	89.46
	0.10C	0.700	6.0227	11.8156	100.26	74.75	23.3408	20.6344	88.40
	0.20C	1.400	6.0162	8.5451	100.15	74.67	23.7861	20.6448	86.79
	0.50C	3.500	6.0065	7.2249	99.99	74.55	24.4212	20.5940	84.33
	0.75C	5.250	5.9762	7.1198	99.48	74.18	24.4775	20.4916	83.72
	1.00C	7.000	5.9380	7.1191	98.85	73.70	24.3436	20.3758	83.70
-30°C	0.05C	0.350	4.8979	17.5462	100.00	60.79	19.2008	15.7285	81.92
	0.10C	0.700	4.9060	12.5917	100.17	60.89	19.6208	15.8273	80.67
	0.20C	1.400	4.8917	11.0017	99.87	60.71	19.9209	15.7832	79.23
	0.50C	3.500	4.8458	10.9032	98.94	60.15	19.8666	15.6073	78.56
	0.75C	5.250	4.7908	10.9447	97.81	59.46	19.6417	15.4358	78.59
	1.00C	7.000	4.7384	10.9658	96.74	58.81	19.4268	15.2829	78.67
-40°C	0.05C	0.350	2.3155	11.5376	100.00	28.74	9.4238	7.4320	78.86
	0.10C	0.700	2.5426	12.1132	109.80	31.56	10.4195	7.4810	71.80
	0.20C	1.400	2.5536	12.4072	110.28	31.70	10.4692	7.4183	70.86
	0.50C	3.500	2.5583	12.4359	110.48	31.75	10.4887	7.4318	70.86
	0.75C	5.250	2.5640	12.5156	110.73	31.82	10.5120	7.4359	70.74
	1.00C	7.000	2.5637	12.5045	110.72	31.82	10.5108	7.4364	70.75

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6.2 Availability of Source Materials for Li-Ion batteries

The Title 3 Technology Investment Agreement (TIA) between Quallion and the US Air Force Research Lab was initiated in September 2006. The purpose of the TIA is to establish a trusted domestic source of spacecraft quality lithium-ion 50Ah true prismatic cells and the raw material for lithium-ion production. Quallion will participate in this TIA with a 23% cost share.

Overall goals for this greater than eight million dollar effort are the establishment of an ensured source of materials to:

- Strengthen the US-owned domestic industrial base for true prismatic, extremely long life cells and batteries for USG satellite use of at least one MWhr/year (approximately 3600 nominal 50 Ahr cells). This will be produced in a clean/dry room at a semi-automated rate of 70 per week.
- Establish US-owned domestic source of LCO cathode materials (200kg/month) for USG satellite use, through a technology transfer agreement with a foreign company.
- Establish US-owned domestic source of anode material MCMB (200kg/month) for USG satellite use, through a technology transfer agreements with Ube Chemical.
- Stockpile the LCO precursor material for future USG satellite cell production use.

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7.0 Findings, Observations, and Recommendations

7.1 Generic Safety, Handling and Qualification Guidelines for Lithium-Ion (Li-Ion) Batteries

7.1.1 Li-Ion Performance Assessment (GRC)

Findings

- F-1.** A database of lithium-ion cells and batteries appropriate for aerospace applications with capacities greater than 1 A-hrs has been created by the battery working group.
- F-2.** The database of lithium-ion cells and batteries is not a comprehensive database of all lithium-ion cells and batteries, rather a compilation of data that was either found or shared from various industry and government partners.

Observations

- O-1.** The majority of batteries used for space applications using Li-Ion batteries that were identified in this study are based on the 18650 HC cells and made by ABSL.
- O-2.** It is unknown if the predominant usage of 18650 HC cells reflects accurately the preference for space battery experience with Li-Ion batteries or if those that used other cells were unwilling to share their data.
- O-3.** Usage of Microsoft Excel, due to its architectural limitations, is difficult to keep up to date and shared with many parties. Additionally, it has limited database functionality to link photographs and other documents with the associated cell and or battery.

Recommendations

- R-1.** It is recommended that the NESC explore migrating the MS Excel data to a more comprehensive database program. (O-3)
- This would maintain a single source for the current database from which all participants would obtain the data and additionally allow the participants to update and add new data as it becomes available.
 - Vendors are motivated to update this database frequently as it would be as source for all NASA to use to obtain Li-Ion data. Database access can be limited to those participating in the study and NASA.

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7.1.2 Generation of a Guidelines Document that addresses Safety and Handling and Qualification of Li-Ion Batteries (GRC)

Findings

- F-1.** A document has been developed containing guidelines on the safety, handling, and qualification of Li-Ion batteries. (Appendix B)
- F-2.** Li-Ion battery technology has not stabilized to a particular chemistry, or design, and testing is still being performed to evaluate safety issues as the technology evolves.

Observations

There were no observations for this task.

Recommendations

- R-1.** It is recommended that all NASA programs considering the use of Li-Ion technology use these guidelines in developing or procuring a Li-Ion battery for aerospace applications. (F-1)
- R-2.** It is recommended that these guidelines be reviewed and revised to incorporate additional lessons learned on a periodic basis. (F-2)

7.1.2.1 Definition of Conditions Required for using Pouch Cells in Aerospace Missions

Findings

- F-1.** Pouch corrosion can be replicated and accelerated in certain cell design by shorting its pouch to the negative terminal of the cell. Two cell designs (LG and SKC) could not be made to corrode by this method. Each of these 2 corrosion resistant cell designs had the following distinguishing features;
- It appears that the pouch-to-tab seals are made with a 3-step process that stabilizes the location of the tabs relative to the pouch, melts the seal material, and then applies pressure to complete the seal. The die press used has sophisticated contours leaving marks not seen on the other cell designs.
 - The tabs were found to be centrally and symmetrically sealed between opposing pouch material layers
 - The multiple and distinct insulating layers exist in the inner side of pouch laminate material and those layers smoothly mix with the tab seal material.
 - Edges (other than the tab seal edge) are sealed with a different sealer.

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- Less excess separator material near the edge and corner seals and that separator material is unaffected by the sealing process.
- F-2.** Electrical isolation of the aluminum layer of the pouch laminate from the negative terminal of pouch cells degrades in the days and hours prior to the initial appearance of corrosion spots. Monitoring this electrical isolation degradation was found to provide advance warning of future visual evidence of pouch corrosion.
- F-3.** Pouch corrosion is only found in the stretched, butter cupped sections of the pouch laminate, consistent with the fact that the electrically insulation layers of the laminate are most stressed and weakened in those areas.
- F-4.** The cell pouch design with the lowest leak rate per Ah, per surface area, per volume and is LG's. The designs from Kokam, Quallion, and SKC also performed well. Each of these good performing cell designs had the following distinguishing features:
- Large and wide tab seal material
 - Only one pouch side is butter cupped (or stretched)
- F-5.** An estimation of the calendar life of a cell design is possible once you know its amount of free electrolyte and its PAIR determined leak rate. The calendar lives estimated for the six cell designs investigated herein varied from 3 to 63 months at ambient conditions.
- F-6.** Similar to past experience, the leak rate of all the cell designs is higher with thermal cycling than with ambient storage, because cell seals are stressed due to differences in thermal expansion of the different pouch laminate layers and tab seal materials

Observations

There were no observations for this task.

Recommendations

Based on the findings of this effort to date, the following recommendations are offered to buyers of Li-Ion pouch cells for long life applications:

R-1 through R-6. During cell design selection process, perform the following design feature examinations and tests to assess hermeticity and susceptibility to pouch corrosion of candidate designs.

- R-1.** Look for uniformity in the placement of the pouch perimeter seals relative to the cell stack. (F-1.)
- R-2.** Polarize the pouch to the negative terminal for several weeks to determine susceptibility to corrosion. (F-1.)

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- R-3.** Obtain a cross-cut examination of the pouch laminate in the flat, butter cupped, and seal areas to determine uniformity of thickness of all laminate layers. (F-1.)
- R-4.** Measure the isolation resistance of each tab seal from the pouch as an indication of poor symmetry within the tab to the pouch seals. (F-2)
- R-5.** Select a design that butter cups only one pouch cell side, not both. (F-4)
- R-6.** Leak test the cell using PA-IR or other technique after exposing it to mission relevant environmental conditions to determine leak rate of the most volatile component of the electrolyte, determine quantity of free electrolyte, and the mass fraction of the volatile component of the electrolyte. From that data, estimate the time that it will take for all the free electrolyte to escape the cell to ensure that it's compatible with application requirements. (F-4)

Task II : Recommendations for Aerospace Applications of Pouch Cells

Pouch cell configuration provides several advantages over conventional Li-ion cells, i.e., with metallic containers, in terms of specific energy, energy density and packing efficiency. Some of the prototype cells of different types have shown impressive specific energies of 160-200 Wh/kg, at least 20% improvement over their counterparts. One limitation pertaining to a widespread use of pouch cells in aerospace applications is the lack adequate robustness in the hermeticity and integrity of the cells, especially upon electrical and thermal cycling and possibly under hard vacuum environments. This characteristic is a function of electrolyte, type of cathode material (which dictates the charge voltage and hence the extent of electrolyte oxidation) and the pouch seal design. Furthermore, this failure is accelerated at high temperatures, for example, cycling at 60°C, showed clear demarcations among various cells tested. Interestingly, SKC gel polymer showed the greatest resilience to the high temperature cycling and may be expected to exhibit similar tolerance to vacuum also. The team also anticipates that the Compact Power cells will perform well under such conditions (testing underway). It is recommended that the selected prototype cells be tested in the anticipated thermal and vacuum environments before hand, before putting them for use. As a diagnostics, the cells may be subjected to an accelerated cycling test at a high temperature, after establishing a correlation between such acceleration and the expected cycle life at room temperature.

7.1.2.2 High Voltage Risk Assessment: Limitations of Internal Protective Devices in High-Voltage/High-Capacity Batteries Using Li-ion Cylindrical Commercial Cells

Findings

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- F-1.** The PTC characteristics varied from manufacturer to manufacturer in their trip currents as well as withstanding voltages. The withstanding voltage of the PTCs implies that there is a voltage limitation.
- F-2.** Diodes placed across series substrings help shorten string lengths and reduce the voltages seen by the cell PTCs during fault conditions.
- F-3.** When cell PTCs are tripped, the heat generation which holds them in their tripped state stresses the cell seals (often detected by odor). Tripping cell PTCs irreversibly increases their electrical resistance by up to a factor of two. Compromised or high-resistance PTCs cause catastrophic failures under overcharge conditions. (Appendices G and J)
- F-4.** The heat generated in a tripped cell PTC was 3.2 to 3.5 W (irrespective of cell manufacturer and load used for trip) which could have been one of the causes for the thermal runaway in a multi-cell battery configuration under unsafe conditions. (Appendix G)
- F-5.** The CID did not protect or underwent incomplete opening and reset under some overcharge conditions. (Appendix J)
- F-6.** In cell banks, two major factors dictated the reaction of the cells to overcharge conditions. These were the charge current and voltage limit of the charger or power supply. For example, 16 cells in parallel went into a thermal runaway under 48 V, 24A conditions as well as 12 V 24A conditions. But they did not go into a thermal runaway under 12 V, 12 A test condition. (Appendix J)
- F-7.** Using excessive charger power supply voltage can cause catastrophic failures if batteries get into an overcharge condition. The difference between the end-of-charge voltage of the module and the charger power supply voltage limit could result in CID arcing if that difference was too large (≥ 50 V for the cells studied). (Appendices H and J)
- F-8.** It was found that in a parallel bank of cells, catastrophic results were obtained if the charge current and the power supply voltage are set at high values. This helps to explain the thermal runaway in cases where the voltage limit and /or charge current were set at a very high value (48 V and 6A for a bank of four cells or 24A for a bank of 16 cells). (Appendix J)
- F-9.** In cell header tests, CID arcing, in the absence of excess liquid electrolyte was found in some cases (30 percent of samples for two types of cells); in the actual cell tests, this arcing did not occur. (Appendices H and I)

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F-10. Electrolyte electrochemical decomposition/reaction occurs on the CID under overcharge condition causing discoloration – possible cause of fire and thermal runaway in overcharge conditions. The CID was found to be wet and discolored in the arcing test with the full cell. (Appendix I)

Observations

There were no observations for this task.

Recommendations

- R-1.** Determine the PTC withstanding voltage and trip current for the cell to be used in battery design by test. Cells from different manufacturer will have different PTC ratings and this information is not provided in a cell specification. (F-1)
- R-2.** In batteries where other design features cannot be used to limit voltage, substring diodes should be used to prevent PTC exposure to high voltages, under fault conditions. (F-2)
- R-3.** The cell PTC should not be compromised (activated or subjected to a condition that causes a rise in its resistance) if needed to be used as safety control. Cell screening for battery build for engineering, qualification as well as flight testing should not cause inadvertent activation of the PTC. Any cells in which the PTC may have been inadvertently tripped should not be used in the fabrication of flight batteries. (F-3)
- R-4.** The heat (3.2 to 3.5W) generated in a tripped cell PTC device must be properly dissipated to prevent its hazardous failure in a multi-cell battery configuration. The thermal dissipation paths for this heat must be analyzed within the battery design and validated to ensure preservation of the cell PTC device's safety feature. (F-4)
- R-5.** The CID cannot be always depended upon as safety control in multicell series/parallel battery designs. To prevent cells from going into an overcharge condition, voltage monitoring should be implemented at a level, which must be defined on a case-by-case basis that would allow reliable and accurate detection and prevention of an overcharge condition of even a single cell. (F-5)
- R-6.** Confirm that the CID safely activates and protects the battery from overcharge catastrophies in the actual flight battery configuration, if the CID is used as a level of safety control. Tests should be run at the module size that the CID is being used as a safety control. (F-6)

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- R-7.** The difference between the charger/power supply voltage limit and the end of charge voltage of the battery should be set as low as the application would allow. At any point during the charging process, including failure modes that result in overcharging, no single cell CID should see a voltage high enough to cause arcing during CID opening. (F-7)
- R-8.** The charge current used to charge a string or a bank should be as low as possible. For charging of cell banks, the total charge current should be limited to a value that would not cause PTC activation in any single cell in the event that the CIDs of all the other cells have opened. (F-8)
- R-9.** Recommend all new cell designs be verified for arcing limits. (F-9)

7.1.2.3 Definition of Safe Limits for Charging Li-Ion Cells

Findings

- F-1.** Li-ion cells upon charge at high rates and/or low temperatures can exhibit a tendency to have metallic lithium deposited on the carbon anode
- This is a result of a deviation from the intercalation process that the Li-ion chemistry was designed to accomplish (in contrast to Li metal systems).
 - Li plating will have deleterious impact on the performance, reliability and maybe even safety.
 - Li plating is dictated by several parameters including the nature of electrode and electrolyte materials and the cell design parameters, especially the relative electrode capacities.
 - Electrolytes that cause poor interfacial conditions at the anode and reduce the intercalation kinetics at two temperatures will favor Li plating.
 - High cathode to anode capacity ratios (or low anode capacity reserves) is likely to result in lithium plating during low temperature charging.
 - Different prototype cells (Yardney, SAFT, Quallion, A123 and SKC) have been found to exhibit different degrees of propensity towards lithium plating as dictated by their chemistry and design.

Observations

There were no observations for this task.

Recommendations

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- R-1.** Li-ion cells upon charge at high rates and/or low temperatures can exhibit a tendency to have metallic lithium deposited on the carbon anode which will have deleterious impact on the performance, reliability and even safety. It is recommended that Li-ion cells and batteries be tested in the expected charge regime and temperature range before putting them in use. (F-1)
- R-2.** Since this characteristic is specific to each cell and dictated by several parameters including the nature of electrode and electrolyte materials and the cell design parameters, especially the relative electrode capacities, it is recommended that such screening is done on each type of cell. (F-1)
- R-3.** As a recommended diagnostics, the cells may be charged at the relevant charge rate and temperature and one may look for the evidence for Li plating in a subsequent discharge, which will be in the form of a voltage plateau about 100 mV higher than normal in the early stages of discharge. (F-1)
- R-4.** It is recommended that some margin is allowed in the charge rates, since the relative electrode capacity ratios may get worse upon cycling, due to a relative faster degradation from the anode. (F-1)
- R-5.** The plated lithium may partly be intercalated, either during the tapered charge mode or in the open-circuit stand, depending on the characteristics of the anode and electrolyte and needs to be studied further. (F-1)
- R-6.** Likewise, the long-term impact of such Li plating, though known to be harmful, needs to be understood. (F-1)

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7.2 Availability of Source Materials for Li-Ion batteries

Findings

No Findings were identified for this sub-task.

Observations

- O-1.** NASA has contributed to the support of the Defense Production Act Title III effort via this NESC supported task. Under this project, a cost share Technology Investment Agreement (TIA) was awarded to Quallion, LLC, Sylmar, California on September 5, 2006. The agreement is managed by the US Air Force Research Laboratory (AFRL/RXM). It will serve to do the following:
- Strengthen the US-owned domestic industrial base for true prismatic, extremely long life cells and batteries for USG satellite use of at least one MWhr/year (approximately 3600 nominal 50 Ahr cells). This will be produced in a clean/dry room at a semi-automated rate of 70 per week.
 - Establish US-owned domestic source of LCO cathode materials (200kg/month) for USG satellite use, through a technology transfer agreement with a foreign company.
 - Establish US-owned domestic source of anode material MCMB (200kg/month) for USG satellite use, through a technology transfer agreements with Ube Chemical.
 - Stockpile the LCO precursor material for future USG satellite cell production use.

Recommendations

The major technical objectives of the project are as follows:

- R-1.** Continue collaboration and cooperation with other government agencies to ensure the availability of quality materials with known performance for use in Li-ion cells.

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7.3 Maintaining Technical Communications Related to Aerospace Batteries (NASA Aerospace Battery Workshop)

Findings

- F-1.** The 2007 NASA Aerospace Battery Workshop convened in November 2007. The workshop was attended by scientists and engineers from around the world, representing both private industry and government entities. The number in attendance was 123, which represented a 10 percent over the previous year's attendance.
- F-2.** Topics covered from the 2007 workshop included ground test and flight results, charge control, and safety for the Li-Ion battery chemistry, flight results for the nickel-hydrogen battery chemistry, and some of the latest work from some of the key aerospace battery manufacturers around the world.

Observations

There were no observations for this task.

Recommendations

- R-1.** Continue conducting Workshops. (F-2)

8.0 Other Deliverables

8.1 Maintaining Technical Communications Related to Aerospace Batteries (NASA Aerospace Battery Workshop)


Presentations from the workshop are posted on the workshop's website soon after the workshop is completed. Further downstream, these same presentations are published on a CD that is distributed to those on the workshop distribution list.

9.0 Lessons Learned

9.1 Generic Safety, Handling and Qualification Guidelines for Lithium-Ion (Li-Ion) Batteries

9.1.1 Li-Ion Performance Assessment (GRC)

After compiling a large amount of cell and battery data it was observed that MS Excel has limitations on both the ability to search for items, the ability to put in links to additional work and pictures and most importantly to open the information up to the

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widest available NASA user community. Additionally, due to the rapidly changing Li-Ion industry, improvements in both cell capacity and chemistry occur often and are reflected in new cell and battery models. A web-based Li-Ion data center would allow cell/battery vendors to update their data as new cells or new performance data becomes available and allow customers to relay their experiences of using the vendor's cells/batteries. Additionally, vendors are motivated to keep a web-based database that is used by NASA to investigate cell and battery options up to date with their latest data. Using a more complete database program and having it be web-based would of provided a better tool for the entire NASA community to find cell and battery information and have it be a dynamic and living document.

9.1.2 Generation of a Guidelines Document that addresses Safety and Handling and Qualification of Li-Ion Batteries (GRC)

Additional work is continuing to determine controls and testing needed for the safe use of Li-ion batteries. In addition, continuing changes in cell chemistry that affect the safe use and handling of Li-ion technology are occurring and will need to be addressed. The guidelines should be revisited and revised in one year to incorporate any newly developed recommendations.

10.0 Definition of Terms

18650	A standard cylindrical cell size where the cell is 18 mm in diameter and 65.0 mm in height.
Accelerated Cycle Test	A test where the cell or battery is charged and discharged under conditions more stringent than those expected in its proposed application in order to produce premature degradation so that normal operating life can be estimated.
Acceptance	A determination that the product meets the design specifications.
Active core	The material in the cell that is undergoing oxidation or reduction during the electrochemical reaction.
Amp-hr	A measure of capacity in Ampere-hours (also indicated as Ah).
Anode	The electrode where oxidation occurs during the electrochemical reaction during discharge.

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Anode to Cathode Ratio	The ratio of the capacity of the anode material in a cell to the capacity of the cathode material.
Arc	An electric current, often strong, brief, and luminous, in which electrons jump across a gap. Electric arcs across specially designed electrodes can produce very high heats and bright light.
Battery	One or more electrochemical cells that are electrically connected.
C/n (or C-rate or charge /discharge rate)	The discharge or charge current that will deliver the rated capacity of the battery in n-number of hours. For example, a 20 Ah cell discharged at a C/2 rate (a rate that will deliver the total capacity of the cell in 2 hours) is discharged at 10 A.
Calendar Life	The maximum allowed period of use of the cell or battery as defined from the date of manufacture of the oldest cell in the battery.
Capacity	The number of ampere-hours that can be delivered by a fully charged cell or battery under the specified conditions.
Capacity Fade	The gradual loss of capacity that occurs with cycling/use.
Catastrophic	Thermal runaway, venting with fire, violent venting with expulsion of cell contents, expulsion of cell from multi-cell module configuration, resulting in loss of mission of life.
Cathode	The electrode where reduction occurs during the electrochemical reaction during discharge.
Cell	A single-unit device within one cell case that transforms chemical energy into electrical energy at characteristic voltages when discharged.
Cell Activation	The addition of electrolyte to a cell that enables the electrochemical reaction to take place.
Cell Balancing	The process of charging and discharging the cells in a battery so that they have the same voltage levels.

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Cell Bank	Cells connected in a parallel configuration (have the same voltage, capacity is additive).
Cell Design	A cell design is built to one set of manufacturing control documents that define material composition, dimensions, quantity, process, and process controls for each component in the cell.
Cell String	Cells connected in a series configuration (voltages are additive; same current is passed through all of them).
Cell Lot	A continuous, uninterrupted production run of cells, which consists of an anode, cathode, electrolyte material, and separator, from the same raw material sublots with no change in processes or drawings. Li-Ion cells produced in a single lot should be procured, stored, delivered, and tested together to maintain single lot definition.
Charge Retention	The fraction of the full capacity of a cell or battery under specified discharge conditions that is still available after it has been stored.
Cold Storage	For batteries that are not in use, is long-term storage where the temperature and humidity environments are controlled, and temperature is below ambient temperature.
Constant Current Mode	Charging or discharging the cell or battery with a non-varying current.
Constant Potential Mode	Charging or discharging the cell or battery using a varying current to maintain a constant voltage.
Corrective Actions	Changes to design processes, work instructions, workmanship practices, training, inspections, tests, procedures, specifications, drawings, tools, equipment, facilities, resources, or material that result in preventing, minimizing, or limiting the potential for recurrence of a problem.
Current Interrupt	

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Device (CID)	A mechanical device within the cell which permanently breaks the connection to the electrode when the cell pressure reaches a design-specific internal pressure.
Cycle	A discharge, where the capacity of the battery is used, and subsequent recharge, where the capacity of the battery is restored, of a rechargeable battery.
Cycle Life	The number of discharge/charge cycles performed by the battery.
Cylindrical Cell	A cell where the electrodes are rolled up and placed in a cylindrical container.
Depth of Discharge	The ratio of the capacity removed from a cell or battery under specified conditions to its rated capacity.
Destructive Physical Analysis	The process of opening up a cell, removing material from it, and analyzing the changes that have occurred.
Dry Life	The maximum allowed period of storage of the cell or battery before electrolyte is added to activate the cell.
Electrode	The location where the electrochemical reactions occur.
Electrode Capacity Ratio	See Anode to Cathode Ratio.
Electrolyte	The medium which transports ions between the electrodes.
Energy	Launch, transfer orbit, and on-orbit battery energy and energy reserve requirements are flowed down from the Electrical Power Subsystem specification for the entire mission life. Battery energy is equal to the integral of the product of discharge current and voltage, where I_d , a positive value, is the discharge current, and V_d , a positive value, is the discharge voltage. The limits of integration are from start of discharge to either the minimum power subsystem battery voltage limit, or when the first cell reaches the lower cell voltage limit, or when a defined time duration is reached. This is a point-in-time energy value that is measured at a defined charge voltage-current profile,

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discharge load profile, and temperature profile. Battery discharge can be accomplished with constant current discharge; however, constant power discharge is the preferred method if it more closely simulates spacecraft power. This is also sometimes called Watt-hour capacity.

$$\text{Battery Energy (Wh)} = \int I_d V_d dt$$

Energy Density	The ratio of the energy output of the cell or battery to its volume, typically in Wh/l.
Energy Reserve	Total amount of usable energy in Watt-hours remaining in a battery, which has been discharged to the maximum allowed DOD under normal operating conditions to either the minimum power subsystem battery voltage limit, or when the first cell reaches the lower cell voltage limit.
Finding	A conclusion based on facts established by the investigating authority.
Formation	Electrochemical processing of an electrode which transforms the active material into a useable form.
Free Electrolyte	Excess electrolyte beyond what is needed to facilitate the electrochemical reaction.
Hermiticity	The effectiveness of the seal of the cell container in preventing leakage.
Intercalation	The insertion of ions into the active material.
Lessons Learned	Knowledge or understanding gained by experience. The experience may be positive, as in a successful test or mission, or negative, as in a mishap or failure. A lesson must be significant in that it has real or assumed impact on operations; valid in that it is factually and technically correct; and applicable in that it identifies a specific design, process, or decision that reduces or limits the potential for failures and mishaps, or reinforces a positive result.
Maximum Expected	

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Operating Pressure	The maximum pressure that pressurized hardware is expected to experience during its service life, in association with its applicable operating environments.
Module (or Battery Module)	A battery module is an assembly of series- or parallel-connected battery cells that are connected (usually in series) to form a battery.
Observation	A factor, event, or circumstance identified during the assessment that did not contribute to the problem, but if left uncorrected has the potential to cause a mishap, injury, or increase the severity should a mishap occur. Alternatively, an observation could be a positive acknowledgement of a Center/Program/Project/Organization's operational structure, tools, and/or support provided.
Polarization	The change of the potential of a cell or electrode from its equilibrium due to the flow of current, which typically results in higher an increase in resistance and degradation of performance.
Positive Temperature Coefficient (PTC) Device	A solid-state device inserted in the cell which heats up when passing higher currents and whose resistance increases with increasing temperature, impeding the flow of current in the cell. When currents return to normal, lower levels, the material cools and resistance returns to normal.
Problem	The subject of the independent technical assessment/inspection.
Procurement Authority spacecraft.	The agency responsible for the procurement of the
Proximate Cause	The event(s) that occurred, including any condition(s) that existed immediately before the undesired outcome, directly resulted in its occurrence and, if eliminated or modified, would have prevented the undesired outcome.
Qualification	The process of verifying that the product can meet the design specifications within the mission operating conditions.

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Rated or Nameplate
Capacity

Measured in units of Ampere-hours or Watt-hours. The rated battery capacity is provided by the battery or cell vendor and is typically less than the actual capacity. Manufacturers usually provide excess capacity over the rated value to compensate for variability within the manufacturing lot and capacity losses expected over the life of the battery.

Recommendation

An action identified by the assessment team to correct a root cause or deficiency identified during the investigation. The recommendations may be used by the responsible Center/Program/Project/Organization in the preparation of a corrective action plan.

Reversal

The changing of the normal polarity of a cell, typically due to overdischarge of the cell.

Root Cause

One of multiple factors (events, conditions, or organizational factors) that contributed to or created the proximate cause and subsequent undesired outcome and, if eliminated or modified, would have prevented the undesired outcome. Typically, multiple root causes contribute to an undesired outcome.

Self Discharge

The loss of useful capacity of a cell or battery due to internal chemical reactions.

Service Life

The service life of a battery, battery module, or battery cell starts at cell activation and continues through all subsequent fabrication, acceptance testing, handling, storage, transportation, testing preceding launch, launch, and mission operation.

Shelf Life Limit


Shelf life limit for a battery, module, or cell is the maximum allowed time from cell activation to launch. This includes any time in cold storage.

Specific Power

The ratio of the power delivered by the cell or battery to its mass, typically in W/kg.

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Specific Energy	The ratio of the energy output of the cell or battery to its mass, typically in Wh/kg.
State of Charge	The ratio of the number of Ah or Wh present in a battery for a defined charge voltage-current profile, discharge load profile, and temperature profile to the rated energy E(Ah or Wh) of the battery, times 100.
	$\text{Battery State-of-Charge (\%)} = [\text{E(Ah or Wh) present} / \text{E(Ah or Wh) rated}] * 100$
Thermal Vacuum Cycling	Discharge/charge of the battery within a vacuum chamber at the thermal conditions that are expected in its application.
Venting	The relief of excessive pressure within the cell case by expelling gases.
Verification	The process of checking that the product meets the specified requirements.
Voltage Clamp	Maintaining a constant voltage during charge by varying the charging current (see Constant Potential Mode).
Wet Life	The maximum period during which a battery can deliver a specified capacity after activation.

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11.0 Acronyms List

AC	Alternating current
Calipso	Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations Mission
CID	Current Interrupt Device
COTS	Commercial-off-the-shelf
dc	Direct current
DEC	Diethyl Ethyl Carbonate
DME	Dimethyl Carbonate
DOD	Depth-of-Discharge
DPA	Destructive Physical Analysis
EC	Ethyl Carbonate
EDS	Energy Dispersion Spectroscopy
ESTA	Energy Systems Test Area
GEO	Geosynchronous-Earth-Orbit
GOES	Geostationary Operational Environmental Satellite
GRC	Glenn Research Center
GSFC	Goddard Space Flight Center
HST	Hubble Space Telescope
ISS	International Space Station
LEO	Low-Earth-Orbit
Li-Ion	Lithium-ion
JPL	Jet Propulsion Laboratory
JSC	Johnson Space Center
MCD	Manufacturing Control Document
MCMB	meso-carbon micro-beads
NASA	National Aeronautics and Space Administration
NESC	NASA Engineering and Safety Center
Ni-H ₂	nickel hydrogen
NSWC	Naval Surface Warfare Center
OCV	Open Circuit Voltage
PAIR	Photo-Acoustic Infrared
PTC	Positive Temperature Coefficient
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
SOC	State of Charge
TDRS	Tracking and Data Relay Satellite

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Appendix I. Current Interrupt Device (CID) Arcing effects in Li-Ion cells

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